STUDIES IN SORPTION

ON

ANODISED ALUMINIUM

by

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PART I.

INTRODUCTION.

Section I.

Aluminium enjoys a unique position, owing to its physical and chemical properties, as a light metal. Since the invention of the electrolytic process of isolating the metal in 1886, the world production of aluminium has risen from 40 tons in 1886 to approximately 600,000 tons in 1938. The impurities in the metal incorporated during the manufacturing processes have a very deleterious effect on its resistance to corrosion. Numerous researches since 1900 have been made to attempt to remove the impurities. As a result, pure aluminium which is more highly corrosion-resistant, can now be produced commercially.

Aluminium possesses a great affinity for oxygen, as shown by the high heat of formation of its oxide. A very thin natural film of aluminium oxide is, therefore, always present on the surface of the metal. Research has indicated that actually it is this thin film of oxide which is responsible for the high corrosion resistance exhibited by the metal and its ability to take up a high polish without tarnishing.

The work done to investigate the nature and properties of the natural film of oxide on aluminium attracted considerable attention and efforts were directed to produce heavier oxide coatings artificially so as to improve on the properties of the natural film. These efforts culminated in the discovery, by Bengough and Stuart (1), of the method of producing anodic films by electrolytic oxidation of aluminium. The process gives a

hard oxide film on aluminium and its alloys under suitable conditions of oxidation and appears to be specific to aluminium, since it is not applicable to the same extent to other metals, such as magnesium. None of the other light metals produces surface coatings with such useful properties or protective effect as aluminium.

The surface films so produced on aluminium serve a wide variety of purposes, such as to provide a 'key' for painting, to afford protection to the metal against corrosion or chemical attack, or to increase the mechanical resistance of the surface. The film has the properties of electrical insulation and shows a rectifier effect. Anodic treatment is also used for brightening or polishing an aluminium surface. The oxide coating possesses a very great adsorptive power, a property with which we shall be mostly concerned in this thesis.

The phenomena associated with the modern processes of anodising were first observed in 1857, but the early patents taken out were for the use of the film in electrolytic rectifiers or condensers. Indeed, workers in the field were engaged for many years on research that had no intentional bearing on anodising as a means of increasing resistance to corrosion, which is perhaps its most important application. G.D.Bengough and J.M.Stuart (loc.cit.) took out the first patent for protecting aluminium and its alloys from corrosion by means of anodic treatment in 1923 and the first patent for colouring the anodic film was also taken out at the same time(2). As others proceeded to experiment with different substances

and conditions, further patents followed, but the original process remains largely unaltered, namely to use aluminium as the anodes in an electrolyte under an applied voltage. Bengough and Stuart are recognised as the pioneers of anodising and their chromic acid process is one of the main processes in use today. In the quarter of a century since the first patent by Bengough and Stuart as many as 175 patents have been granted, dealing with the anodic oxidation of aluminium and its alloys, and the dyeing of anodised aluminium. Most of the main processes are, however, now free from patent restrictions.

The process of anodic oxidation of aluminium consists primarily of passing direct electric current through a suitable electrolyte with aluminium as anode and lead or carbon as cathode. This process differs fundamentally from other electrolytic processes because the anode itself takes part in the chemical reaction and is slowly eaten away, while the cathode only conducts the current. Alternating current is also used sometimes, but the direct current is the most commonly employed. A wide variety of electrolytes and conditions of carrying out the process have been proposed, each giving an anodic film suitable for a specific applicatinn. However, there are three processes more widely used than the others:-

(a) <u>The chromic acid process</u>. This was the first to appear and has held the ground in modern practice due to certain advantages. Three per cent. chromic acid is the electrolyte most generally used though 5 per cent. and 9.5 per cent. are also sometimes employed. The recommendation of Bengough

and Stuart (1) is to use 3 per cent. chromic acid and raise the voltage from 0 to 40 volts during the first 15 minutes and then hold it at 40 volts for 35 minutes, followed by an increase to 50 volts over 5 minutes with a total treatment time of 60 minutes at $40^{\circ}C \pm 2^{\circ}$. A simplified operation, using 3 per cent. chromic acid and raising the voltage from 0 to 45 volts over 5 minutes with a total treatment time of 60 minutes at $45^{\circ}C$, was suggested by Pullen (3). This method was used later on in the present investigation. This process yields opaque films of 7 - 8μ average thickness. The dyed film lacks some of the lustre of shades on the sulphuric acid film and as the penetration of dyestuff is small, the fastness properties are poor.

(b) The sulphuric acid process. First patented by Gower and Stafford in 1927 (4), this process is perhaps the most popular process at present. It is the most extensively used in U.S.A. and forms the basis of the Alumilite process (5). An electrolyte containing about 15 to 25 per cent. sulphuric acid is used and has the advantage that low voltages and low temperatures may be used (10 to 15 volts at 20° to $25^{\circ}C$.). Colourless and transparent films of 0.007 m.m. average thickness are obtained on pure aluminium in 30 minutes' treatment and they are ideal for dyeing. Clear shades of good fastness properties are obtained. This method was also used in the earlier experiments of the present investigation.

(c) The oxalic acid process. This process, patented by Hojin, Rikagaku Kenkyujo in 1924 (6), was fairly widely

used in Japan and Germany, but its use is now decreasing. The process is carried out in a 5 per cent. electrolyte at a temperature of 30°C. using 40 volts or even higher voltages. The use of direct current gives light straw coloured films, while the alternating current gives brass yellow to bronze coloured films of 0.030 m.m. average thickness. The colour of the film interferes with the dyed shades, though they possess good fastness properties. The cost of the electrolyte, which is gradually oxidised at the anode, is higher than of the other processes.

Direct current is generally employed in these processes, but there is a limited use of alternating current for special purposes, as well as the use of alternating current superimposed on direct current.

Effect of the base metal:- The colour of the anodic films obtained by the different processes described above is that on pure aluminium, but the colour of the film is greatly affected by even minute quantities of alloying constituents, or impurities (7). When the constituents are uniformly dispersed in solid solution in aluminium, the oxide film has a uniform appearance as in the case of pure aluminium (8). Free alloying constituents which may or may not be dissolved or oxidised by the anodic treatment have a pronounced influence on both the anodising process and the coating formed. The presence of traces of silicon tends to produce grey to brownish shades, while relatively large amounts of it in aluminium will give brown to black coatings. The anodic films on alloys

containing copper have not only a yellow cast but are the thinnest, since the copper compounds produced at the anode are more soluble in the electrolyte than aluminium oxide (9). This shows that the thickness of the anodic film is also dependent on the composition of the base metal. The thickest films are obtained on pure aluminium. Apart from the chemical composition, the physical condition of the metal surface has an effect on the appearance of the films. The appearance of the coated surface can be given many variations by suitable treatments before coating, such as buffing, etching or sandblasting.

Action of electrolyte:- The nature and concentration of the electrolyte play a very important part in determining the type of film obtained during the anodic process. It is chemical and not electrolytic properties which are responsible for this; for, electrolytically all of them behave in the same way. Different electrolytes have different solvent action on the film, while some have none at all. Boric acid or its salts, for example, give only very thin impervious coatings as in this acid practically no solution of the coating occurs and the flow of current rapidly comes to a standstill. Such coatings are valueless from the point of view of improved corrosion resistance or absorption of dyes but are quite useful in certain electrical apparatus, such as condensers and rectifiers.

If, on the other hand, chemical attack dissolves the coating at a rate faster than that at which it is formed, it is evident that no film would result, but this action leaves a

smooth and bright surface. This fact is utilised in processes of electrolytic brightening of aluminium surfaces for making reflectors.

An ideal electrolyte, therefore, should have a moderate solvent power for the oxide coating, so that it will help the porous oxide coatings to be formed and maintain the conduction of the current and, consequently, the continuity of the process. The thickness of the film continues to increase so long as the rate of its formation exceeds the rate of dissolution. Finally a stage is reached when solution of the film just balances its formation; thereafter its thickness remains constant. The three electrolytes described above fulfil this condition. It has been observed, however, by Mason and Sunder (10) that less coating is dissolved by sulphuric acid when the current is passing through and it is being formed than when the coated aluminium piece is merely dipped in the electrolyte. The explanation offered by them is that the high concentration of aluminium sulphate within the pores causes a decrease in the solubility of the coating.

In general, it may be said that the greater the concentration of the electrolyte, the greater the solution of the coating in it.

Effect of temperature, time and current density:- Temperature of the electrolytic bath plays an important part in the nature and amount of the coating formed. Mason and Sunder (loc.cit.) observed that each $5^{o}C.$ rise in temperature results in a considerably lower value of equilibrium between the rate

of formation and the rate of solution of the coating, so that above 50°C. coatings can no longer be obtained. The pores in the coating are funnel-shaped, narrowing towards the interior. The temperature of the electrolyte affects the taper of the pore walls. At low temperatures the taper is slight but it is proportionately greater at higher temperatures, so that the size of the pore increases at the outer surface with rise in temperature. This would probably result in the breakdown of pore walls on the outer surface and a soft layer. This may be the reason why the abrasion resistance of the coating decreases as the temperature of the electrolyte increases. It would also explain the fact that oxide coatings formed at higher temperatures sorb dyes more readily (10).

The thickness and the amount of coating formed are almost directly proportional to the current density and this relationship is nearly independent of ordinary variations in concentration and pH of the bath, though it varies for different alloys. Tarr, Darrin and Tubbs (11) found that a similar relationship exists between current density and amount of aluminium oxidised. Temperature has a marked effect on current density. Increasing the temperature increases the current density and hence the amount of coating formed. This would probably be balanced out by increased solution of the coating at the higher temperature.

Increase in thickness of the coating is a function of time, but the ultimate thickness is affected by the solvent action of the electrolyte. As the oxidation progresses, the

thickness of aluminium decreases until the metal is so thin that it melts due to the great resistance. This interrupts the passage of the current with the result that in the interior of the film, more or less minute fragments of the metal will always be found.

General properties of the anodic film:- It has been shown how films of widely differing properties can be produced by electrolytic processes and how the type of current, the current density or voltage, the nature, concentration and temperature of the electrolyte, the duration of treatment and the composition of base metal all contribute to the differences in properties. It was this flexibility of the process to suit many purposes that made it at once popular and commercially successful.

The density of the films is found to be in the neighbourhood of 3 gms. per c.c.(12). It is interesting to note, however, that crystalline alumina has a density of about 3.9 to 4.0 gms. per c.c.

Anodic films are much harder than the metal, though hardness of a film decreases along an axis perpendicular to the metal surface. The hardness of the film gives the surface the property of abrasion-resistance.

Some films possess greater flexibility than others, but flexibility decreases as the film thickness increases.

The dielectric constant of films was found to be about 7.45 by different methods, while both for corundum and precipitated Al_2O_3, it varies from 12 to 12.3 (9).

The films possess a very high resistance to heat and have good electrical insulating properties. The adhesion of the film to the base metal is so good that special chemical or electrochemical means are necessary to separate them.

Highly reflective and bright surfaces are obtained by anodic treatment in a solution of fluoboric acid (13) or of sodium phosphate and carbonate (14).

The films possess high porosity and good absorptive power. This may be considered a disadvantage, since film may take up liquids which will attack the base metal, thus reducing the protection against corrosion. On the other hand this property offers many advantages. The film absorbs dyes, giving coloured surfaces. It can also take up photosensitive materials or water repelling and electrically insulating substances. The films have proved valuable as a basis for the adhesion of paints and lacquers.

The films have excellent corrosion resistance, because the porosity may be reduced by subjecting the film to a process called "sealing" which makes it impermeable and non-absorptive. This may be done by boiling in water (15), by treatment in hot solutions of nickel or cobalt acetates (16) or by "choking" the pores with solution of oils or waxes in suitable solvents (8). Sealing also prevents the anodised articles from taking up stains and gives the films a necessary resistance to handling.

Of the properties of the film mentioned above, one that is very widely used and has come to be very important now is

porosity. This enables the film to be coloured different colours. The film absorbs certain types of dyes and holds them with greater or less fastness. It is quite impossible to leach out some dyes from the films once they are absorbed. This led to speculation about the forces that keep these dyes attached to the film. A large amount of work to produce various fancy effects by absorption of dyes, mostly covered by patents, has appeared, but no serious attempt has been made to elucidate the mechanism of sorption of dyes or other organic compounds by the anodic film. The present investigation was therefore undertaken to throw light on this mechanism.

Section II.

Since in the present investigation the anodic film as the sorbent plays a very important part, the mechanism of its formation and structure will be briefly considered. A brief review of similar sorbents, e.g. fibres, will also be given.

Mechanism of film formation:-

The mechanism responsible for the film formation in the anodic process is fundamentally different from that of other electro-deposition processes. The electrolyte contains no aluminium ions except those resulting from the unavoidable chemical dissolution of the anode, and hence the oxide film can grow only at the expense of the base metal. Therefore, although the films produced by different processes may differ considerably as regards their physical properties, it is now generally agreed that they are constitutionally similar in each case.

From an investigation of the factors governing the formation of anodic films on aluminium in an alkaline hydroxide solution, Lilienfeld, Nieh and Goldman (17) came to the conclusion that the primary reaction is that between the metal and hydroxyl ions to form an "embryonic layer" of $Al(OH)_3$; when the potential gradient across this layer becomes sufficiently high, the $Al(OH)_3$ is dehydrated and alumina is added to the visible, or so-called dielectric layer. However, it has not been observed with any degree of certainty that this stage of hydration occurs at any definite stage of the reaction. The

suggestions often found in the literature that the aluminium salt primarily formed at the anode is hydrolysed and precipitated as $Al(OH)_3$, which migrates electrophoretically to the anode, where it is dehydrated to alumina, do not appear to be tenable. Hydrolysis is most unlikely to occur in the conditions obtaining at the anode in a strongly acid electrolyte and the positively charged $Al(OH)_3$ will not migrate to the anode. Setoh and Miyata (18) consider that an active layer is formed by direct union between the metal and oxygen, which is liberated at the anode as a result of electrolysis and penetrates the pores in the existing layer; thus the film continuously grows from the active layer. The oxide film is thus formed at the surface of the metal and may therefore be considered "to grow outwards". If we consider, say, electrolysis in sulphuric acid, there will always be present as a result of passing the current in the solution of sulphuric acid, $SO_4^=$ and $O^=$ ions at the anode. The lower discharge potential of the $O^=$ ion (+1.23 v) allows it to be discharged preferentially to the $SO_4^=$ ion (+1.9 v) with higher potential. The oxygen is in the extremely active form in which the $O^=$ ion exists immediately after being discharged and combines with aluminium which is also in a highly active state, to form aluminium oxide. The presence of water and the electrolyte results in the incorporation of both to some extent in the film.

These considerations indicate quite definitely that the film formation is purely a phenomenon of direct oxidation. The reaction may be expressed in formulae as:-

$$2\,Al + 3\,O = Al_2O_3$$

or $$2\,Al + 3\,O + H_2O = Al_2O_3.H_2O$$

The film formed then dissolves in the electrolyte, a dibasic acid in this case, which can be represented as:-

$$3\,H_2R + Al_2O_3 = Al_2R_3 + 3\,H_2O;$$

or $$3\,H_2R + Al_2O_3.H_2O = Al_2R_3 + 4\,H_2O;$$

The specific volume of the oxide is somewhat higher than that of the metal from which it is formed. Fig.1 represents the variations in total thickness, as found by Wernick (24), of a sheet of aluminium as it was progressively anodised in moderately dilute sulphuric acid.

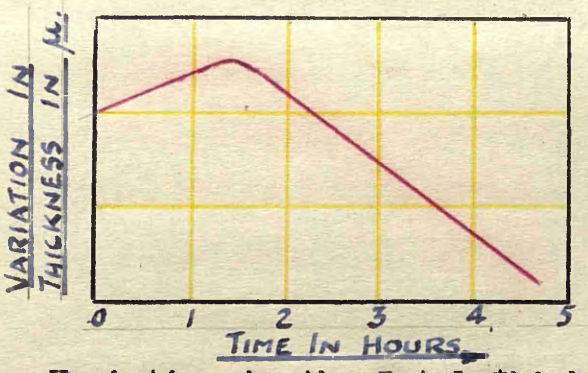


Fig.1. Variation in the total thickness of an aluminium sheet with progressive anodisation.

The total thickness, as can be seen from the figure, undergoes an increase up to about 75 minutes and then decreases.

Fig.2 outlines the individual phases in the formation of the film. As the oxide layer increases in thickness, the base metal becomes thinner and the metal/oxide interface is, therefore, shifted progressively in towards the bulk of the anode, though the total thickness is greater than the original thickness of the metal at the start (Stages a, b, c). As

the process continues and electrolyte dissolves the film, a stage is reached when the total thickness is equal to the

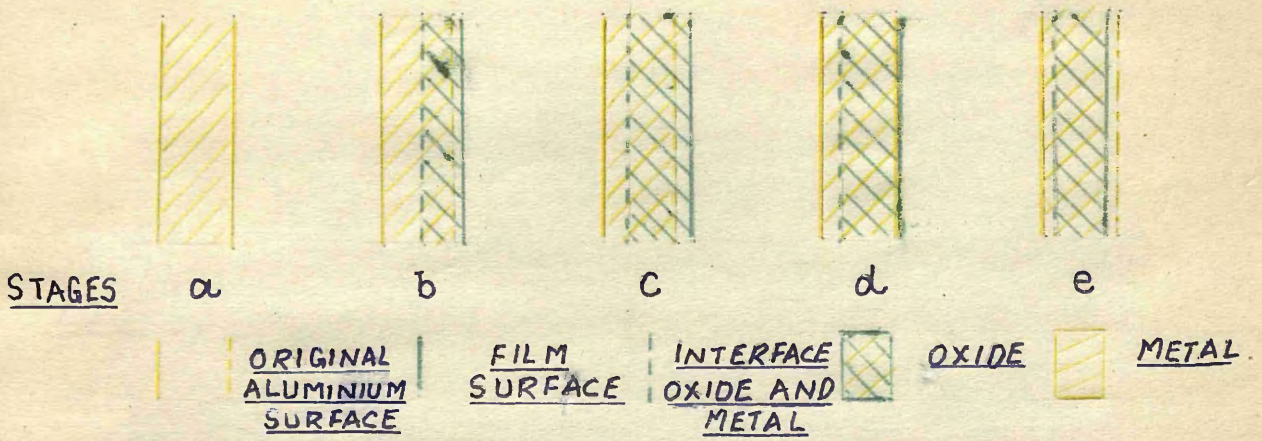


Fig.2. Progressive phases in film formation.

original thickness (Stage d) and at a further stage it is less than the original. The extent of this dissolution is common to all anodic processes and depends on the electrolyte. Solution occurs to a greater extent with sulphuric acid than with chromic acid.

The actual formation of the anodic layer is probably a highly complex process taking place in at least two distinct stages. The first stage appears to be the formation of a thin layer strongly adhering to the base metal over which the further growth of the film, constituting the second stage, takes place. The existence of this thin layer in an anodic film was shown by many workers. Zlotowoki (19) suggested that the electrostatic capacity of anodic films was due to a thin non-porous film, the thickness of which increases exponentially with time. Baumann (20) found that the film was divided into three distinct zones. Next to the metal surface is a compact layer of γ-aluminium oxide which is retained with high fields. Above

this is a high pressure gas layer. The pores of this film were filled with electrolyte. Cuthbertson (21) used the cathode-ray oscillograph to obtain information about electrical conditions at the surface of the electrodes and found that current-voltage curves are closed loops with a constant shape indicating constant capacity and hence constant thickness of a thin active layer. Unlike Zlotowski, he did not find any increase in thickness of this layer with time. In his opinion the mechanism of electrolytic oxidation is similar, in chromic, sulphuric and oxalic acid baths but the larger and more perfect loops obtained with chromic acid indicate its superiority to other electrolytes in giving more satisfactory films. Tomashov (22) suggested that beneath the porous thick film a thin continuous film exists and the action of electrolyte on its surface makes it porous. Examination of films by these workers with the electron microscope confirmed the porous structure, which is the direct result of the mechanism of their growth. On the other hand Burwell jr. and May (23) in an attempt to measure the permeability characteristics of the films came to the conclusion that the main obstruction to permeability is a comparatively impervious barrier layer and it appears as if the film is not entirely penetrated by pores.

Mott (118) proposed a theory to explain the formation of protective oxide films in air on metals like aluminium and it provided reason for their limiting thickness. The theory can be substantially applied to electrolytic formation of the films. Mott assumes that the formation of the oxide takes place by the

diffusion of metal ions and electrons through the oxide layer. If the electrons have enough energy to diffuse to the outer surface of the oxide layer, metal ions will combine with oxygen at the surface to form new layers of oxide. Electrons can penetrate an insulating layer up to a distance of about 50 Å without receiving any energy of excitation. Mott's theory is based on this effect known as quantum mechanical tunnel effect. Later on, however, he (119) proposed another theory in which he assumed that during electrolytic oxidation, oxygen ions are adsorbed on the surface and a strong electric field is set up. The solubility of metal ions in the oxide at temperatures considered is very small for their passage but the ions can migrate under these strong electric fields. By both treatments, he arrives at the value of work function required for the diffusion of the metal ions and electrons, which are comparable and lead to the limiting value of the oxide films usually found. He states, however, that more experimental work would be needed to determine which is correct. Scott Anderson utilising the same ideas (25) has put forward a very comprehensive theory to explain the mechanism of electrolytic oxidation of aluminium. He has shown that only the thin compact layer of aluminium oxide next to the metal is active so far as the growth of the film is concerned. Al^{+++} ions with a radius of 0.5 Å easily diffuse through the barrier under the influence of an intense electrical field, which is of the order of 10^7 volts/cm. When sufficient space has been created, $O^{=}$ ions with a comparatively large radius of 1.3 Å move in.

One out of three Al^{+++} ions diffuses through the oxide layer into the electrolyte, where it forms a soluble salt with the acid, and the other two combine with $O^{=}$ ions to form Al_2O_3. Thus the oxide layer grows with a total thickness greater than the original thickness of the metal and with the barrier layer always in good contact with the metal, which explains why the films are so tenaciously attached. According to previous theories, if all the aluminium was converted to aluminium oxide, the "efficiency ratio", which is the ratio of the oxide formed to the weight of aluminium reacting, is given by the formula

$$Al_2O_3/2\ Al$$

and will be equal to 1.89. According to Scott Anderson's theory the efficiency ratio will be given by

$$N\ Al + Al_2O_3/3\ Al$$

where N is the fraction of diffusing Al^{+++} ions that have not penetrated to the solution before the first penetrates the barrier layer, and will equal unity. Therefore the highest efficiency ratio will be 1.59 , which is nearer the actual values found by Edwards and Keller (26) than the value 1.89 . In the case of boric acid, the migrating Al^{+++} ion does not dissolve in the electrolyte but is precipitated as oxide and forms a part of the film. Thus all the aluminium leaving the sheet enters the oxide film: two thirds by the electrochemical process and one third by chemical precipitation, but as the thickness of the film increases, the electrical field falls to such a low intensity that the Al^{+++} ions diffuse very slowly and the growth practically stops. The value of the efficiency

ratio will be in the neighbourhood of 1.89. According to this theory, current is carried by outward diffusion of Al^{+++} ions and the inward shift of $O^{=}$ ions. This theory appears to explain all the outstanding characteristics of the electrolytic process and the film formed.

Structure and composition of the anodic film.

As has been mentioned, the structure of the film depends upon the nature of the electrolyte used. Coatings formed in sulphuric, chromic and oxalic acids are porous and adsorptive while those formed in boric acid are substantially impervious and non-adsorptive, the films formed in the former being constituted of more or less evenly spaced pores perpendicular to the surface of the film. Photomicrographs taken by Edwards and Keller (27) with optical and electron microscopes suggest a porous open tube-like structure of the film, while the same authors elsewhere (26) point out that microscopic examination of cross-sections of coated aluminium prepared by a special metallographic technique developed by them indicates that the oxide has a cellular structure. Mahl (28), using an electrostatic electron microscope to investigate the structure of the anodic films, found that the film which has no structure when of very low thickness becomes granular with increasing thickness, but the grains do not exhibit a crystalline nature. They "must be interpreted as variations in thickness (pores) occurring during the growth of the film", based on the pores formed in the initial layer. Burwell and May (23) measured the permeability characteristics of these

films by studying the rates of diffusion of salts, and of osmosis through the film, used as a membrane. These data and studies with the electron microscope indicate that the anodic film is penetrated by numerous sub-microscopic pores. They calculated the diameter of these pores to be about 110 Å and their number about 1.55×10^{11} per sq. cm. in films formed in sulphuric acid electrolyte. Rummel (34) states that the diameter of the pores, which are fairly regular and perpendicular to the surface, is of the order of 10 Å. Huber (29) considers that because the numerous pores are in random arrangement in a film, its structure corresponds to that of a "mixed body" consisting of parallel cylinders of an isotropic material penetrating through the whole thickness of another isotropic material, and, using an expression correlating the structural birefringence of such a "mixed body" with the volume percent. of each material (30), he calculated the pore volume at the metal/oxide interface as about 4 percent., and at the oxide/electrolyte interface as about 16 percent.

Many authors who have studied the structure of the films by X-rays state that the oxide has an amorphous structure, while some say that the films are crystalline. Edwards and Keller (26) found them to be amorphous as far as can be determined by X-ray and electron diffraction methods. Pullen (31) agrees with this view but adds that the observation is probably due to the crystals being too small to give a pattern. Taylor, Tucker and Edwards (32) carried out a variety of experiments and found that when the film was formed at a potential of above

about 100 v., the oxide gave an electron diffraction pattern corresponding to that of γ-alumina, which indicated that high electrical stress appeared to be favourable to the formation of an ordered oxide lattice. They also found that it was not the characteristic of any particular electrolyte to yield a crystalline coating, for they obtained crystalline coatings with a variety of electrolytes. Harrington and Nelson (33) made an electron diffraction study of anodic films and found that those formed at room temperature usually gave diffuse patterns while the randomness of the structure decreased at higher temperatures. The composition of the film varies from alumina to alumina monohydrate. Sutton and Willstrop (42) found little change in weight when they heated a piece of anodised aluminium from 50°C. to 600°C. and it regained the original weight in a few hours on exposure to air. They also heated a similar piece in vacuo to a temperature of 1200°C., when any water contained in the film will react with the metallic aluminium with the evolution of hydrogen. The volume of hydrogen evolved was not appreciable and was practically the same as the volume of the gas evolved from the same weight of unanodised aluminium subjected to similar experimental procedure. They therefore concluded that the film consists of oxide and does not have an appreciable water content. On the other hand, Treadwell and Obrist (43) claim that the film shows a dielectric constant of 7.58 , which suggests that water contained in the oxide is bound in the form of a uniform hydrate.

A study of the large amount of published work on oxides of aluminium and their hydrates indicates clearly the confusion that prevails in this field. Many workers have at various times claimed the existence of various forms of the oxides and hydrates of aluminium and at other times some of the recognised ones have been named differently by other authors. Edwards et al.(35) state that since the advent of X-ray methods of identification it has been possible to classify the oxides. They have proposed to use a nomenclature for hydrates similar to that being used for oxides. Accordingly they come to the conclusion that three oxides - α -Al_2O_3 , β -Al_2O_3 and γ -Al_2O_3, and four hydrates - α and β trihydrates and α and β monohydrates exist. Weiser and Milligan (36) carried out an X-ray study on aluminas precipitated under a wide variety of conditions and found that only two hydrates - a trihydrate (gibbsite) and a monohydrate (diaspore) - exist. Edwards and Tosterud (37) consider this to be untenable in view of the X-ray and chemical evidence they possess. They have confirmed the findings of Edwards et al.(35) described above. Both the groups of authors confirm the existence of γ -Al_2O_3 , as postulated by Barlett (38). Later, Weiser and Milligan (39) in view of the evidence presented by other authors agree that two more hydrates - α -$Al_2O_3.3\,H_2O$ (bayerite) and γ -$Al_2O_3.H_2O$ (böhmite) also exist. It appears that γ -$Al_2O_3.H_2O$, described by these authors is the same as α -$Al_2O_3.H_2O$ described by Edwards et al.(35, 37).

Belwe (40) investigated aluminium oxides by electron

diffraction and found that the electrolytic films consist of finely crystalline γ-Al_2O_3. These findings corroborated those of Verwey (41). Taylor (44) investigated the changing X-ray pattern and adsorption activity of a sample of γ-$Al_2O_3 . 3\ H_2O$ (gibbsite) when it is dehydrated by heat treatment. He found that changes took place in the order trihydrate $\longrightarrow$ monohydrate $\longrightarrow$ γ-alumina $\longrightarrow$ α-alumina. All the stages gave distinct crystalline X-ray patterns except the γ-alumina, which gave a diffuse pattern. The work of Jellinek (45) on the relation between heat treatment and crystallite size and of Riley (46) on heat treatment of magnesium carbonate and of ferric hydroxide, suggest that during the dehydration process developing patterns which indicate the progressive growth of crystallite size within the particle are obtained, and that a crystalline body can break down producing a highly disordered state of transition and exhibiting modified physical and chemical properties. Taylor (loc.cit.) concludes, therefore, that "γ-alumina is not a completely defined entity like the γ-monohydrate (böhmite) or α-alumina (corundum), but a transitional product in a heat-controlled solid reaction, at first highly disordered but rearranging to an orderly state as the reaction proceeds." The adsorption activity, measured as the weight of dye (waxoline Blue CS) adsorbed by unit weight of alumina, was found to be directly related to the degree of conversion to γ-alumina, hence to the state of disorder. When the alumina was wholly in the form of monohydrate, the activity was negligible. Anhydrous alumina was extremely active and

hence it follows that the crystallites were very small. It would, therefore, be understandable that the X-ray pattern of such a phase would be diffuse. The increase in activity can be explained by assuming that with progressive dehydration, comparatively large monohydrate crystallites break down to small crystallites thus increasing the available surface area. Further heat treatment helps the growth of crystallites with the result that the activity is again reduced. From this work it appears that the activity is a function of the surface area of the material as well as the atomic arrangement in the particle having an incompletely developed crystalline structure. As has been mentioned, the X-ray pattern of the oxide in the film is diffuse and conforms more to that of -alumina than any other oxide or hydrate of aluminium. Again the other oxide of aluminium - α-Al_2O_3 - is formed at high temperatures (above about 900°C.) The sorption activity exhibited by the alumina of the film is quite high - probably higher than that found to be possessed by γ-Al_2O_3 as determined by Taylor (loc.cit.). It seems likely, therefore, that the anodic film mostly consists of γ-alumina, probably with a very minor quantity of monohydrate depending upon the conditions of oxidation. This might be the reason why some workers have found the oxide to possess an X-ray pattern of crystalline nature. Mutch (47) was able to distinguish only the γ-monohydrate pattern in samples of alumina heated to 400°C. for several days and containing 4-6% of water, probably because the diffuse pattern of γ-alumina was obscured by the sharply

defined pattern of the monohydrate. It is quite likely that a similar thing could happen in this case and if under certain conditions of oxidation a fairly large amount of monohydrate was formed, the ultimate X-ray pattern would appear crystalline and thus mislead. Pullen (31) has some evidence to show that the films formed in chromic acid electrolyte are practically anhydrous alumina. It has also been observed that the films decrease in adsorption activity if stored for a long time. This is probably because small crystallites grow with time, though very slowly, the temperature being low, thus reducing surface area and hence activity.

The films also contain substances adsorbed from the electrolyte and impurities from the metal, if pure metal is not used. The film obtained in chromic acid electrolyte contains less than 0.1 per cent. chromium and hence is purer than the films from sulphuric acid and oxalic acid, which contain about 13 per cent. sulphates and about 3 per cent. oxalic acid respectively probably, present as basic compounds (31).

On boiling the film in water, a marked decrease in adsorption capacity occurs (15). This "sealing", as it is called, can also be effected by treatment in other substances such as oils, waxes and their solutions in suitable solvents. Harrington and Nelson (33) observe that treatment of anodised or unanodised aluminium in water at temperatures above $80^{\circ}C$. produces a thin layer of bohmite - γ -$Al_2O_3.H_2O$. The reduction in permeability is attributed by Edwards (8) to the growth of crystalline aluminium monohydrate. A detailed

investigation by X-ray diffraction and chemical analysis of anodic films after boiling in distilled water was made by Pullen (31). It demonstrated a distinct crystalline structure which agreed with the X-ray pattern of α-monohydrate. When the film was ignited, the loss in weight calculated as water was found equivalent to two molecules. He, therefore, suggests that the film, when boiled in water, is transformed into α-monohydrate, holding a molecule of water in the lattice. When such films are heated, the "lattice" water can easily be lost and part of the monohydrate is converted into γ-alumina according to the temperature at which it is heated, and thus the film should acquire its activity again. This has been observed to be so during the present investigation.

Dyeing of anodic film:-

Since the discovery of Bengough and Stuart (2) that the anodic films could sorb water-soluble dyes, a large amount of work has been done on the subject, much of which is found in the patent literature. Most of the work is purely empirical and of a practical nature. Some firms have marketed selected brands of dyes suitable for dyeing of anodic film. A method of printing anodised aluminium surfaces has also been described (49). Jenny (9) discovered and developed the method of using anodic films as a medium for permanent photography by sorbing light sensitive materials into the pores of the film.

Henley (50) has described the classes of dyes with which the film can be coloured and has enumerated the factors on which

the choice should be based. Hill (51) has investigated the fastness and other properties of over thirty-five dyes and classified them in different grades, "excellent", "very good" etc. Gill (52) has made an extensive survey of available dyes with regard to their level-dyeing properties and their fastness to light, heat and cold and hot water. Rhael and Summers (159) recommend the careful preparation of the dyes and accurate control of time and temperature of the anodising bath to prepare standard strips for colour comparison, because the depth of shade is proportional to the quantity and quality of the anodic film. Haller (160) compares the dyeing of oxide film with the sorption of dyes on alumina. He found that both were dyed the same shade uniformly by acid dyes, while the basic dyes did not dye the film but produced a "zoning" effect when the alumina was shaken up with them and allowed to stand. The heavier particles settled down undyed and the finer particles were dyed and settled as a coloured layer above, on standing. He suggests from this that the particle size may be of some importance in dyeing. However, once the anodic film has been dyed, washing with alcohol or any organic solvent will not leach out the dye, while the dyed granular alumina can be easily stripped of dyes by organic solvents. No mechanism of dyeing of the film has been proposed except that certain acid and mordant dyes capable of forming lakes might be doing so by forming such lakes with the aluminium. However, no quantitative work has been reported or conclusive evidence produced to substantiate this statement and hence it should be regarded

more or less as a speculation. It is, however, interesting to note that the patents (161) ( ) describing the methods of dyeing anodic films state that the presence of groups OH and NH_2 is essential to success when dyeing from aqueous solutions of the dyes.

Co-ordination complexes of dyes:-

As mentioned earlier, it has been suggested in the literature that mordant dyes might be forming metallic co-ordination complexes with aluminium when the anodised metal is dyed with such dyes.

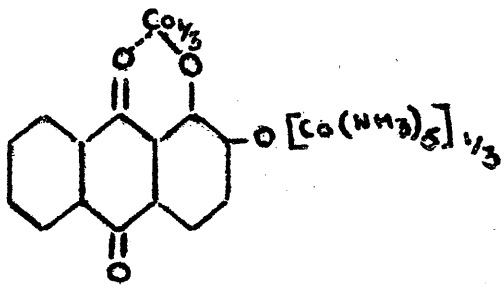
Detailed and extensive investigations by Morgan and his co-workers (94) on cobalt lakes and by Drew and his co-workers (95) on copper, chromium and aluminium lakes have thrown much light on the structure of such metallic complexes.

Werner (96) suggested that the chemical valency of elements can be variable and that the affinity may be distributed over the spherical surface of the central atom, round which all the other atoms associate. The number associating thus is referred to as the "co-ordination number" of the atom. Werner's theory has now been clearly explained by the electronic theory of valency.

Werner also described in the same way the structure of many metallic complexes, and satisfactorily explained their properties.

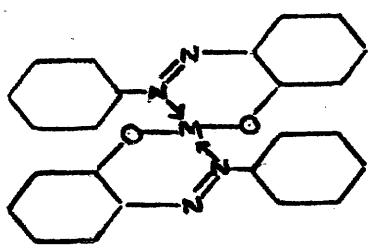
Morgan (loc.cit.) found that a lake of alizarin formed

from a cobaltammine salt has the following constitution:-



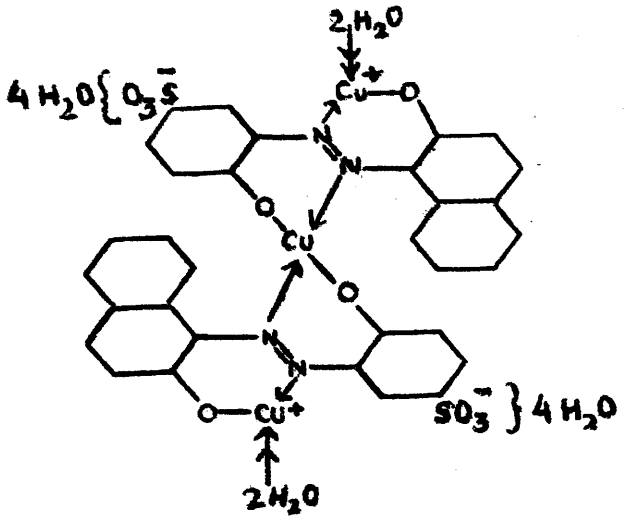
The two-fold co-ordination of one of the cobalt atoms by a principal and a subsidiary valency gives considerable stability to the complex. Morgan called such complexes 'chelate' compounds.

Drew and Landquist (95) found that divalent metals like copper, nickel and zinc form metallic complexes with o-hydroxy-azo compounds, having the following general structure



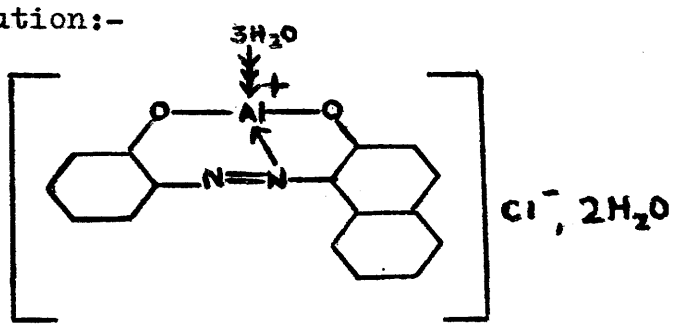
Drew and other co-workers could not prepare lakes from such azo bodies and trivalent metals, like chromium and aluminium, or quadrivalent metals like vanadium. Hence they came to the conclusion that a single o-hydroxyl group in the molecule of an azo dye is not sufficient to hold the metal atom in stable combination. They observed later (loc.cit. 1940) that o:o'-di-hydroxy azo compounds containing sulphonic groups form metal complexes with copper in which both the nitrogen atoms of an azo group are co-ordinated to a metallic atom, which

showed that both the nitrogen atoms can remain co-ordinatively saturated. The complex had the following structure

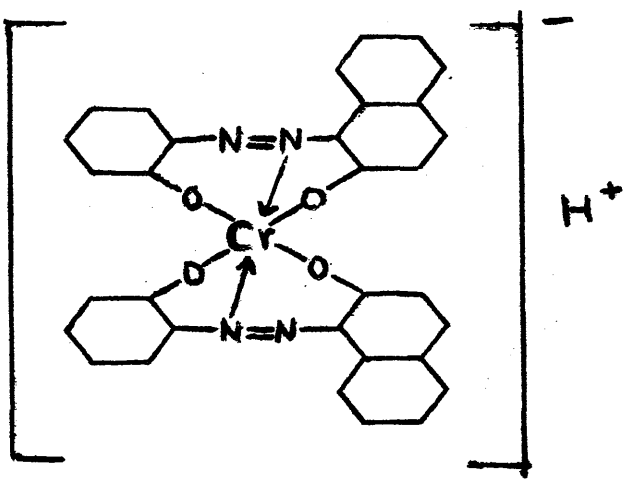


They suggested that probably each hydroxyl of the o:o'-dihydroxy azo dyes is more acidic in character than the hydroxyl of the monohydroxy azo dyes. Morgan also observed that the reason why 1-hydroxyanthraquinone does not form stable metal complexes is probably that it is not sufficiently acidic and the general acidity of the molecule must be increased by introducing another acidic group, preferably in the ortho-position, since a meta-hydroxyl group would not affect the acidity sufficiently to produce a stable lake.

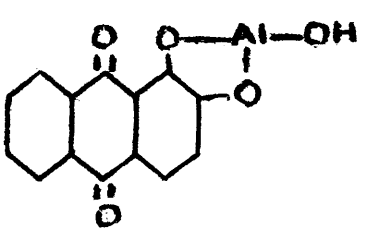
Aluminium gives a complex of the following structure with o:o'-dihydroxy azo dyes such as o-hydroxybenzeneazo-β-naphthol, in alcoholic solution:-



This compound is soluble in water, but on boiling in water loses part or whole of its co-ordinated water, chlorine which was formerly ionically linked then probably becomes co-ordinately attached and the complex becomes insoluble in water. Drew and Fairburn have found that in the case of chromium, the complex takes up one more molecule of the azo dye and forms an anhydrous acidic complex:-

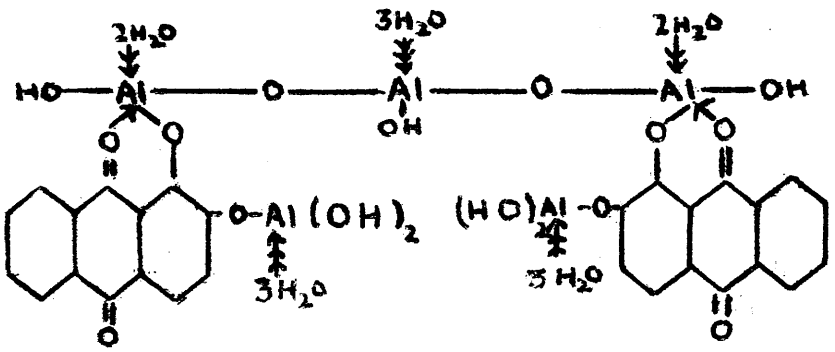


Liebermann (97) suggested that aluminium formed with alizarin a derivative of the formula:-

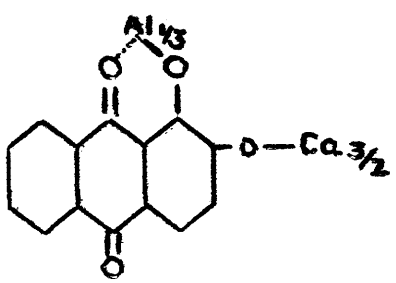


He does not seem to have obtained any substance of this kind. Though many subsequent authors have accepted this formula, both Morgan and Drew came to the conclusion that the metal is co-ordinately attached to the carbonyl and the adjacent hydroxyl groupings, while the remaining hydroxyl in the 2-position is sufficiently acidic to attach a further metal atom

under suitable conditions, though this could be easily removed or replaced. Thus Drew et al. assigned the following formula to the alizarin-aluminium complex:-

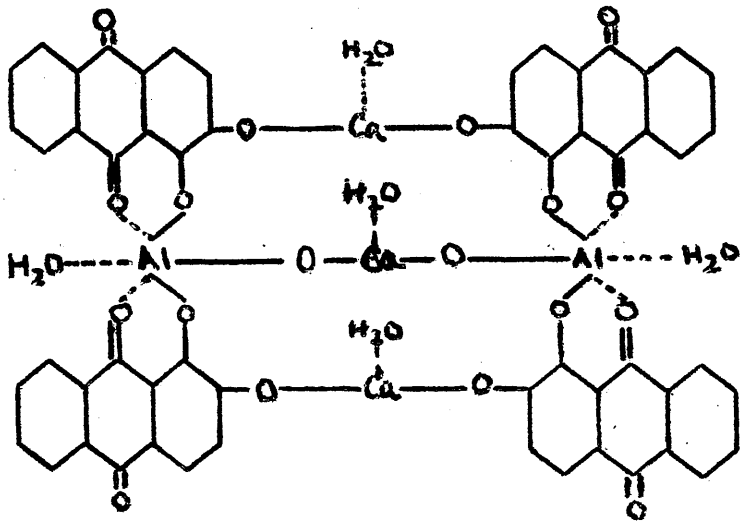


The Turkey-red lake will probably have calcium instead of aluminium in the 2-position. From the analogy of cobalt complexes, Morgan and Main Smith suggested the following structure for the Turkey-red lake:-



Haller (102) has investigated the formation of the alizarin red lake and found that though aluminium and calcium alizarate, either alone or in mixtures are sensitive to metallic salts, their double compound is not affected by treatment with these salts. Fierz-David and Rutishauser (103) found that the lake contained alizarin, aluminium, calcium and water in the proportion of 4 : 2 : 3 : 5 and hence probably had the following

structure:-



The complex easily loses three molecules of water when heated, turning black in colour. The two remaining molecules of water cannot be removed even at 600°C. On exposure to the atmosphere it regains the water and the red colour of the lake returns.

This work indicates that the lakes are definite chemical compounds. This view was questioned by Biltz and Eltescher (98) who found that while a hydrous oxide of iron forms ferric alizarate with alizarin, chromium does not form any such compound. Bull and Adams (99) investigated the iron-alizarin lake and concluded that it is a ferric oxide-sodium alizarate adsorption complex. Williamson (100) came to a similar conclusion about the aluminium-alizarin lake. Weiser and Porter (101) have studied the mechanism of the formation of alizarin lakes with hydrous oxides of iron, chromium and aluminium. They came to the conclusion that the formation of the lakes from sodium alizarate baths is due to adsorption of dye anion by the oxide. They observe that the colour of the

alumina-alizarin lake is due to the adsorption of alizarate radicals on the aluminium atom of the oxide.

It is thus evident that though a large amount of work has been done to investigate the mechanism of colour-lake formation, nothing definite has been established. Doubt exists as to whether it is an adsorption process or chemical combination. The exact position of metallic atoms in the co-ordination complex is not fully known. As most of the satisfactory dyes for anodised aluminium belong to this class of mordant dyes, it was evident that an attempt should be made to elucidate the mechanism of their sorption on anodic film, which might throw light on mechanism of lake-formation.

Theories of dyeing textile fibres.

A very large amount of work has been reported on investigations to determine the mechanism of dyeing natural and synthetic fibres and many theories have been put forward to explain the observed facts. Though the aluminium oxide of the film as a substrate is probably less complex than the fibres, it appears that the forces which play their part in attraction and attachment of a dye molecule to the film are perhaps similar in nature to those involved in dyeing fibres. It is, therefore, thought desirable to review briefly the work on the dyeing mechanism of fibres under this section.

In the dyeing of a fibre, the kinetics of the dyeing process and the affinity of the dye for the fibre are of very great importance. In considering the process from the point of view of both these factors, the structure of the fibre and

the dye will play an important part. All fibres undergo swelling when placed in water and they sorb dyes when in this swollen state. Fibres are believed to contain both crystalline and amorphous regions. The dyes are probably unable to penetrate the crystallites, and they will have to make their way through the "pores" or sub-microscopic capillaries of the amorphous regions linking the oriented crystallites. In an unswollen state, these "pores" are too small for the dye particle to penetrate, but when the fibre is placed in water and swells, the pore-size increases, and the dye particle is then able to diffuse towards the centre of the fibre (53). The particle size of the dye is thus important also. Much experimental work has been carried out to determine the particle size of direct dyes and acid dyes in solution, but the results have been rather inconclusive. It has been generally accepted that levelling acid dyes are less aggregated than direct dyes, though the degree of aggregation varies from dye to dye and decreases with rise in temperature and with increasing dilution. It increases, however, in presence of electrolytes like common salt. Valko (54), on the basis of the results of his diffusion experiments, states that some acid dyes (e.g. orange II) are molecularly dispersed. He found that their aggregation was not influenced by temperature to any appreciable extent. Orange II, Orange 2G and Metanil yellow are dispersed as single ions at 25°, 60°, and 90°C. while other dyes which are partly aggregated do not exceed the size of three dye ions at 90°C. (55). It appears that direct dyes are not dispersed

in uniform particle sizes in solution, but consist of a poly-dispersed mixture of particles of all sizes from a single molecule to large aggregates in dynamic equilibrium (56). As the particles of the smallest size are sorbed by the fibre, the bigger aggregates break down to restore the equilibrium.

The next important point in the study of the kinetics of sorption is the attraction of the dye molecule to the fibre surface. Gee and Harrison (57) put forward an electrical theory of dyeing in 1910 in which they stated that fibres acquire electrical charge in water and attract or repel dye ions according to the nature of this charge. Neale (58) has recently elaborated this theory. The electrical forces which play a part in the dyeing mechanism are of two types. One type is responsible for covalent or hydrogen bonds and acts over short distances of less than 5 $\mathring{A}$. The other type, which is effective over distances of about 100 $\mathring{A}$, can be considered as an attraction or repulsion between the dye ion and the fibre. All textile fibres have a negative electric potential in neutral solutions, while the dyes in solution dissociate into ions carrying electric charges of opposite nature. The colour ions of acid and direct dyes carry negative charges while those of basic dyes have a positive charge. Strong support to this theory is given by the evidence of observations that in neutral dyeing of fibres like cotton, wool and silk, the colour ions are only attached to the fibre while the other counterparts carrying opposite charges are only loosely held around to maintain electrical neutrality

but have no specific affinity for the fibres nor are they attached to their internal or external surfaces (58). To bring a colour ion of valency n up to a fibre surface with a potential ψ_o volts, will require an energy $ne\psi_o$ electron-volts. This is supplied by the thermal agitation of the system. A certain fraction of the colour ions which reach the surface is strongly attached to it by the operation of the short-range forces forming hydrogen bonds or some similar linkage, if the dye and the fibre have suitable groups or configuration to enable these bonds to form. The affinity of the dye for the fibre can, therefore, be varied by changing the constitution of both the dye and the fibre. The effect of the long-range electrostatic forces can be varied by varying the surface charges of the fibre or the dye, for example, by adding a neutral salt to the dyebath, which reduces the negative potential of the fibre, or by using a dye with less highly charged ions, such as one containing fewer sulphonic groups in the molecule. Daruvala, as quoted by Neale (loc.cit.Table 1), has clearly demonstrated this by the measurement of surface potentials of undyed natural and synthetic fibres by the electrokinetic method in sodium chloride solution. On the other hand, a dye having a positively charged colour ion is helped by these forces to become attached to the fibre and the addition of salt decreases the attraction between the dye ion and the fibre.

Other factors such as the structure of the fibre and the affinity of the dye for the fibre and effect of these in

particular cases will be considered in more detail below.

Cellulosic fibres:- The structure of cellulose has now been established as consisting of ß-glucose units joined together by oxygen bridges in 1:4 positions to form linear macromolecular chains of up to about 2000 units.(162). These lie more or less parallel to each other, forming crystalline regions, here and there interspersed by amorphous regions. The permeability of these amorphous regions is important in connection with dyeing phenomena. The diameter of the pores in this region, when swollen in water, is between 20 - 100 Å at room temperature (56, 59). When the average dimensions of a typical direct cotton dye molecule, e.g. Sky Blue FF (length 27 Å, breadth, about 10 Å, negligible thickness) are compared with this, it becomes evident that only single molecules or very small aggregates can diffuse into the fibre. The determination of particle sizes of dyes and pore sizes of cellulose have therefore received much attention. Haller and his collaborators (60) came to the conclusion that the penetration of dyes and mordants is dependent upon the particle size, which must be less than 50 Å, and they developed the theory of the dependence of substantive dyeing on the degree of dispersion. Lenher and Smith (61) found that dyes having particles of diameter greater than an optimum value of 35 - 40 Å at 25°C were not readily sorbed by cotton, though they considered, however, that the actual process of dyeing or equilibrium sorption of dyeing is not affected by the mean particle size of the dye because, as the smaller

particles are sorbed, the larger ones break down to restore the equilibrium. The rate of sorption, however, decreases with increase in mean particle size.

The available surface area in cotton cellulose has been estimated at about 2×10^6 sq.cm.per g., though this figure may be only approximately correct.

The detailed work of Neale and his associates has shown that dyeing is essentially a process of diffusion and follows approximately the course predicted by Fick's Law, which states that the rate of diffusion $\frac{ds}{dt}$ of a dye at any point is proportional to the concentration gradient, $\frac{dc}{dx}$, at that point, or

$$\frac{ds}{dt} = -K\frac{dc}{dx}$$, where K is the diffusion constant

Neale and Stringfellow (62) applied the following equation, first developed by McBain (63) and later used by Hill (64):-.

$$\frac{D_t}{D_\infty} = 1 - \frac{8}{\pi^2}\left[e^{\frac{-\pi^2 Kt}{b^2}} + \frac{1}{9}e^{\frac{-9\pi^2 Kt}{b^2}} + \frac{1}{25}e^{\frac{-25\pi^2 Kt}{b^2}} + \ldots\right]$$

where D_t and D_∞ are the amounts of dye sorbed at time, t, and at equilibrium respectively, b is the thickness of the sheet and K is the diffusion constant. They found that the sorption values calculated from this equation agreed very well with the observed values. Observation of cross-sections of progressively dyed cellophane discs under the microscope has given support to the diffusion theory. It has shown qualitatively that dye gradually spreads from the surface to the centre in the cellophane as expected; and within the

experimental error, the dye distribution is in agreement with calculation. Rate of dyeing determined in different thicknesses of cellophane sheets showed that the time required to reach a definite degree of saturation is proportional to the square of half the thickness of the sheet, which is in conformity with Fick's Law. However, of course, as mentioned earlier, the agreement of the diffusion of dye with that predicted by Fick's Law will only be approximate. Neale and Garvie (65) have found that the diffusion constant calculated according to Fick's Law varies with the concentration of the dye and they suggest that their experimental observations are better represented by the equation

$$\frac{ds}{dt} = -K' . c^{0.5} . \frac{do}{dx}$$

where K' is a new constant and c is the concentration of dye. This is probably because the "apparent" diffusion constant of a dye, which depends upon the partition coefficient, varies from the surface to the centre of the fibre. Boulton and Morton (66) obtained a sigmoid curve for the plot of sorption against the square root of time, whereas, according to diffusion theory, the curve should be a straight line at first, falling off later. However, these deviations, probably due to electrical effects, are not very important and for all practical purposes the dyeing of cellulose should be regarded as a diffusion process.

The diffusion constant of a dye in water has a higher value than in cellulose, thus demonstrating the importance of the rate of diffusion of dye in cellulose as well as the pore size of

cellulose and the minimum particle size of dyes in solution. Increasing the temperature increases the rate of diffusion, but decreases the equilibrium sorption. Both chemical and physical variations in cellulose also affect the rate of sorption. The concentration of dye and the presence of a foreign electrolyte also affect the diffusion process, which may be closely predicted by the application of the Donnan equilibrium equations, the diffused dye molecule being regarded as a non-diffusible ion within the membrane. The saturation value of dyes on cellulose roughly agrees with the amount for a unimolecular layer on the available surface.

This last-mentioned fact lends support to the adsorption theory, which states that direct dyes are merely adsorbed on the cellulose surface. The cause of this adsorption and the mode of attachment of a dye molecule to the fibre has been the subject of much investigation. It is now generally accepted that hydrogen bonds are formed between hydroxyl groups of the cellulose and the oxygen or nitrogen atoms of the dye. Investigations on the substantivity of dyes and its dependence on the spatial arrangement of hydrogen bond-forming groups in the dye molecule lent support to this theory. Strong support on the thermodynamic side came from the calculation of heats of sorption of direct dyes on cellulose, which agree with the formation of two such bonds (67, 68). Ellis and Bath (69) have demonstrated, by infra-red measurements, that, in cellulose itself practically all the hydroxyl groups are involved in hydrogen bonds between adjacent cellulose chains, while the

aggregation of direct dyes in solution can also be explained by the assumption of formation of hydrogen bonds between polar groups such as amino or hydroxyl groups of the dye molecules.

Meyer (70) had earlier laid the foundation of the theory of substantivity by supposing that substantive dyes possess a linear chain molecule and thus can be held closely to the cellulose molecule by mutual residual valency forces. Paine (120) by constructing scale models of dyes showed that substantive dyes do possess a linear structure, while non-substantive dyes possess a structure which does not fit well to the cellulose molecule. He pointed out that in substantive dyes groups such as azo, ethylene and amide links appear at regular intervals of e.g. 10.8 Å, which corresponds fairly well with the repeat pattern of the cellulose chain (10.3 Å). Another condition for the substantivity of a dye was recognised to be coplanarity of structure, i.e. all the benzene rings in the molecule must be flat in one plane. Steric hindrance offered by two methyl groups in the ortho-ortho' positions to the diphenyl link in the "meta" isomer of Benzopurpurine 4B, prevent the structure from becoming coplanar and result in the loss of substantivity. Rose extended the work of Paine, (121), and put forward a co-ordinated account of substantivity. He characterised all groups which impart substantivity to a dye as either electron donors or proton donors and showed that the spacing of these groups should be suitable for forming hydrogen bonds with the hydroxyl group of the cellulose molecule. He concluded that at least two hydrogen

bonds between fibre and dye molecule are required to ensure substantivity. As mentioned earlier, this has been confirmed by recent work (67, 68).

The dyeing of cellulose may then be described as follows:-

In solution, the dye is dissociated into oppositely charged ions. The colour ions exist in a dynamic equilibrium of particles of all sizes from a single ion to aggregates of several. The single ions or very small aggregates are adsorbed on the surface of the cellulose, being helped or opposed by electrostatic forces, and the energy is provided by thermal agitation. Larger aggregates break down to smaller particles to restore the disturbed equilibrium. From the outer surface layer, dye ions diffuse into the interior of the fibre through sub-microscopic pores formed by the swelling of the fibre in water, at a rate approximately predicted by Fick's Law. This rate of diffusion is, however, very slow compared with diffusion in water, but it is important in determining rate of dyeing. Once the dye ion is inside the fibre, it is assisted by short-range electrical forces to form hydrogen-bonds with hydroxyl groups of the cellulose molecule and the substantivity or otherwise of the dye will be determined by the spatial arrangement of polar groups and the linear coplanar structure of the dye molecule. If these are suitable, the dye will form hydrogen-bonds. The addition of electrolyte, or alteration of groups in the dye molecule will alter the electrical charge on the fibre or dye and thus increase or decrease the mutual attraction. After a period of time depending upon the

temperature of the dyebath, and the concentration of electrolyte and of dye, a completely reversible equilibrium is attained. The distribution of dye at equilibrium and particularly the effect of electrolyte can be explained quantitatively in terms of a Donnan equilibrium.

Though the kinetics of the dyeing process have been studied in great detail for many years, the affinity of a dye for a fibre and the energetics of the process have only very recently been investigated. Peters and Vickerstaff (71) define the affinity as "the standard change in chemical potential accompanying the adsorption process" and arrive at the following formula, which allows ready calculation of affinities, heats of reaction and entropy changes of a dyeing process.

$$-\frac{\Delta F^{o}}{R\,T} = \ln\left[D_f\right] \cdot \left[Na_f\right]^{z} - \ln\left[D_s\right]\left[Na_s\right]^{z} - (z+1)\ln V$$

where ΔF^{o} is standard change in free energy

R, gas constant

T, absolute temperature

$\left[D_f\right]$, dye anion concentration in fibre

$\left[Na_f\right]$, sodium ion concentration in fibre

$\left[D_s\right]$, dye anion concentration in solution

$\left[Na_s\right]$, sodium ion concentration in solution

z, basicity of dye

V, apparent volume of cellulose available for dye sorption.

Marshall and Peters (68) have used this equation to calculate affinities, heats of dyeing and entropy changes of several dyes

on different cellulosic fibres. They have shown that these values are independent of the origin of the cellulosic fibre. Thus while they have confirmed the hypothesis of the previous authors that the difference in dyeing behaviour observed in various cellulosic fibres is due to differences in physical structure of the fibres, the energetics involved in the dyeing process are fundamentally of the same nature.

When the system is not in equilibrium, the affinity at the commencement of dyeing, ΔF , can be calculated from the equation

$$-\Delta F = \Delta F^{o} + RTl_n\left[Na_f\right]^z \cdot \left[D_f\right] - RTl_n\left[Na_s\right]^z \left[D_s\right]$$

The calculations from this equation clearly demonstrate the effect of the basicity of the dye (z) and the electrolyte concentration, as shown by Peters and Vickerstaff (71). The predictions of affinities at the commencement of dyeing, based of the above equation, have been fully borne out by dyeings from binary mixtures of dyes, where, the dyeing conditions being identical, the dye with the greater affinity should be preferentially sorbed.

An investigation of sorption of dyes on cotton in absence of an electrolyte shows that isotherms, instead of passing through the origin as theoretically predicted, intercept the dye-on-fibre axis. This suggests that in cotton a small number of sites for which the dye has high affinity are present, and in spite of the absence of electrolyte these sites adsorb the dye strongly. Later on the less active sites take up the dye. This supports the observation that the last

traces of a direct dye sorbed by cotton cannot be removed by repeated washings by water (72). These active sites may be ionic in character and may probably consist of positively charged basic groups demonstrating great attraction for dye anions.

Protein fibres:- The most representative member of this group is wool, which has been the subject of a large amount of work. The dyeing of wool, therefore, will be considered under this section.

The amphoteric character of protein fibres has been recognised for a long time, but detailed knowledge of the structure of the wool fibre is largely due to the classical work of Astbury (73) and Speakman(74). We now know that wool is built up of micelles lying parallel to the axis of the fibre and consisting of long folded parallel peptide chains linked together by cystine and salt linkages, which keeps the molecular chains more or less in one plane. These planes themselves are held together lengthwise by hydrogen bonds or weak forces such as van der Waals forces. The micelles are probably lamellar in shape, about 200 Å thick and 2000 Å long. The intermicellar space has pores, of the order of 6 Å in the unswollen state and about 50 Å when swollen in water, through which dye molecules penetrate the fibre. The internal surface area of a wool fibre is of the order of 1×10^6 cm^2/g. Recent researches by Grälén and his collaborators (75) have shown that the outer surface of the wool fibre, known as the cuticle, is surrounded by a very thin smooth membrane, which they have called the

"epicuticle". This is responsible for the low friction of dry wool fibres.

Knecht (83) proposed and Fort (76) developed the present chemical theory of wool dyeing, which has been proved basically correct as a result of detailed work by Speakman and his associates, and Elod. According to this theory wool on immersion in the bath first combines with colourless acid to form a salt , which is followed by slower formation of a dye-acid salt. This may be expressed by the equations

$$\vdash \overset{+}{N}H_3 \cdot \overset{-}{O}OC \dashv \; + \; HCl \rightleftharpoons \vdash \overset{+}{N}H_3\overset{-}{Cl} \; + \; HOOC \dashv$$

and

$$\vdash \overset{+}{N}H_3\overset{-}{Cl} \; + \; \overset{+}{Na}\overset{-}{D} \dashv \rightleftharpoons \vdash \overset{+}{N}H_3\overset{-}{D} \; + \; NaCl$$

Elod (77) has confirmed this by experiments on the dyeing of wool with Crystal Ponceau R, Thiocarmine B and Sulphorhodamine T, from dyebaths which contained hydrochloric acid. He has measured quantitatively the replacement of Cl^- ion in the wool fibre by the dye anion. On account of the behaviour of wool protein in acid solutions, the capacity of wool to sorb acid alone should be quite interesting. Speakman (78) has demonstrated that acid sorption by wool is a function of the p_H of the bath in which the wool is placed and not of the molar concentration of acid. He has also established that the maximum acid combining capacity of 1 g. of wool is 0.82 ml of N-acid at p_H 1 , which corresponds fairly closely with the number of amino groups in wool. It is quite evident then that the maximum acid combined with dyed wool will be less than that

combined with undyed wool. That this is the case was proved by Elöd (77) by measuring the amounts of acid taken up by wool dyed with 2.5% , 5% and 10% , respectively of Crystal Ponceau R . He found that the acid taken up by wool dyed in this way was,within experimental error, proportionally less than that taken up by undyed wool. Speakman and Stott (78) have demonstrated that deaminated wool has a much reduced capacity for combination with acid and whatever is left is probably due to imino groups in the peptide chain. All these facts can be explained by Donnan's theory if it is assumed that the fibre forms the membrane and $R\text{-}NH_3^+$ ions formed by ionisation of the amino groups of the side-chains in the acid solution are the non-diffusible ions. (79). According to this hypothesis, however, wool cannot be dyed in neutral or alkaline baths, yet a large number of dyes are known to dye wool from such baths. Goodall (80) suggested that these dyes were more aggregated in solution and corresponded more to the direct dyes. It has been shown that these dyes form a group of unlevel dyeing dyes. The reason for this involves considerations of the particle size of the dye and the pore size of the swollen wool. Goodall and Hobday (81) have shown that acid dyes are sorbed by wool from neutral baths in the form of their sodium salts. Valko' (55) has suggested that the mode of attachment of dyes in this case is through hydrogen bond-formation between the peptide chains of the wool and the hydroxyl or amino groups of the dye. As mentioned earlier, the aggregation of dyes in solution is a manifestation of the strong residual valency

forces, which are also responsible for the dyeing phenomena and Valko' suggests that the residual valency forces in the dyes cause such strong affinity for wool that a tendency to unlevel dyeing results. All wool dyes do not fall into the two classes of level-dyeing (or non-aggregated) and unlevel-dyeing (or aggregated) types, but they form a continuous series ranging from one type to another. It is therefore quite likely that in the majority of dyeings both types of mechanism are active. This view has received support in the work of Skinner and Vickerstaff (84) who observed that at p_H 1.2 wool can sorb more dye than is required to saturate all the basic groups present in it.

Gilbert and Rideal's treatment of the subject (85) differs from that of Speakman and his associates in the assumption that the fibre contains identical numbers of positive and negative sites possessing the same properties, and the adsorbed ions are free to occupy any site, irrespective of whether adjacent sites are occupied or not. They suppose that equal numbers of anions and cations are sorbed to maintain electrical neutrality. Lemin and Vickerstaff (86) have used this treatment to derive an expression for the change in standard chemical potential of the dye during sorption on wool, which would form a convenient means of determining the affinity of the dye for the fibre in quantitative terms.

Neale (58) has explained the levelling action of salts in wool dyeing by arguing that the positive charge acquired by the amphoteric protein fibre in acid is reduced by the presence of

salt. Consequently the electrostatic attraction for negatively charged colour ions is also reduced, thus assisting levelling.

Nylon:- Nylon is formed by the condensation of stoichiometric proportions of hexamethylenediamine and adipic acid, according to the following equation

$$HOOC\cdot(CH_2)_4\cdot COOH + NH_2\cdot(CH_2)_6\cdot NH_2 \longrightarrow$$

$$HOOC\cdot(CH_2)_4\cdot\left[CO\cdot NH\cdot(CH_2)_6\cdot NH\cdot CO\cdot(CH_2)_4\right]_n\cdot CO\cdot NH\cdot(CH_2)_6\cdot NH_2$$

Polymerisation proceeds until a long chain with a molecular weight of about 10,000 - 12,000 is built up, leaving, as shown in the equation, free carboxyl and amino groups at the respective ends. The fibre has crystalline and amorphous regions. There are no pores and it does not swell in water.

Peters (87) has shown that at p_H values of 3 - 6, the mechanism of dyeing nylon appears to be similar to that of wool, the only difference being that there are fewer basic sites in nylon as compared with wool. Skinner and Vickerstaff (84) agree with this view and state that nylon appears to contain 0.05 milliequivalents of basic groups per gram of the fibre, while wool has about 0.7 milliequivalents per gram. Thus it is clear that at the p_H range mentioned, dye is sorbed primarily on the amino groups at the end of the chain. Peters also observed that at lower p_H values (< 3), the dye is sorbed on nylon in greater amounts and he suggested that weakly basic amide groups in the chain were responsible for this. Carlene, Fern and Vickerstaff (88) agree with this suggestion and state that, as Harris and Sookne (89) have observed, the peptide groups in nylon must be positively charged at p_H values

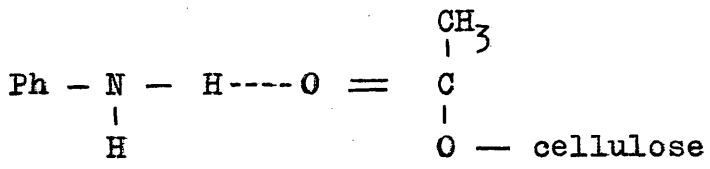
below 2.5 , due to the absorption of hydrogen ions on them. Vickerstaff et al. have obtained strong support for their argument from work on undrawn nylon. They observe that when the dye sorbed exceeds in amount that required to saturate the amino groups in the fibre, the fibre cannot be "drawn" because of the steric hindrance offered by attachment of the dye molecules to the amido groups, which prevents slippage of the polyamide chains past one another. They also suggest that dispersed cellulose acetate rayon dyes are attached to the nylon fibre by hydrogen bonds between the dye molecule and the carbonyl oxygen of the amide groups. These forces are comparable to those existing between the polyamide chains. Nylon is a well-oriented fibre and the dichroic effect observed in nylon dyed with dispersed dyes supports this view. Further support to this view is given by the fact that if the nature of the amino groups at the end of the chain is altered by chemical treatment, the ability of the fibre to take up dispersed dyes of aminoanthraquinone type is not interfered with (93).

Cellulose acetate rayon:- The X-ray examination of the fibre indicates that some small crystallites are present. The fibre has very small pores and does not swell much in water. Kartaschoff (90) showed, by means of photomicrographs that dye, which was initially attracted by electrical forces and formed a thick layer on the surface, vanished later on, dyeing the fibre uniformly. This he attributed to the fact that the dye was dissolved in the fibre. This was confirmed by observation that the fibre was dyed by mere contact with dry dye powder.

In a later work, Vickerstaff and Waters (91) could not detect any electrical attraction between the fibre and the dye particles in the aqueous dispersion. They conclude that the dye particles strike against the fibre surface, by thermal agitation, and because the dispersion contains a mixture of particles of all sizes, smaller - sub-microscopic- particles attach themselves to the fibre surface, which thus dissolves them. Some of the larger particles or aggregates break down to primary particles when they strike the fibre. They demonstrated that the dye dispersion contains such small particles by enclosing the dispersion in a "Cellophane" bag and putting it in water alongside an acetate rayon hank. The acetate rayon hank was evenly dyed by dye particles streaming out of fine pores in the cellophane. These authors also disproved the suggestion of some workers that the dyeing is an adsorption process, by the observation that the quantity of dye taken up by the fibre is not a function of concentration of dye but of the weight of dye in the bath. Dispersions containing large particles dye the fibre very slowly, but increasing the degree of dispersion increases the rate of dyeing.

The mode of attachment of the dye to the fibre has, however, not been indicated. Detailed investigation by Marsden and Urquhart (92) on the sorption of phenols by acetate rayon has indicated that the attachment may be by hydrogen bonding. Calculation of energy of reaction reveals values lower than is usually associated with a hydrogen bond, but the behaviour of acetate rayon towards phenol, o-nitrophenol and p-nitrophenol

lends strong support to this assumption. The fibre exhibits no dichroic effect and hence it is supposed that dyes are not sorbed on the main cellulose chain. The suitable polar group of a dye molecule could form a hydrogen bond with the carbonyl oxygen of the acetyl side chain, as shown below:

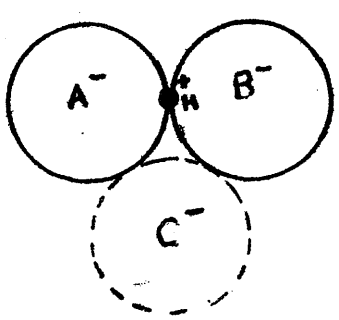


This view of the mechanism can be reconciled with the earlier views of a solid solution of the dye in the fibre by imagining the hydrogen-bond as a "solvating agency".

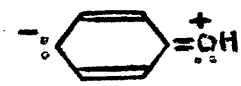
The hydrogen bond:- The review of the work done to elucidate the mechanism of dyeing textile fibres, given in the preceding pages, has abundantly demonstrated the importance nowadays attributed to the part played by the hydrogen bond. It is suggested that the long chains within the fibre may be cross-linked by these bonds. The dye molecules or ions in solution are presumed to aggregate under forces of attraction manifested in the hydrogen bond. The mode of attachment of a dye molecule to the fibre, in many cases, is supposed to be a hydrogen bond. During the present work, the mechanism of attachment of dye to the film in some cases is also attributed to the hydrogen bond. It is, therefore, proposed to consider here the conditions of its formation and properties.

Since the first mention of the hydrogen bond by Moore and Winmill (104) and Pfeiffer (105), it has been the subject of

much study in a large number of organic and inorganic compounds. Huggins, in an unpublished work in 1919, and Latimer and Rodebush (106) recognised its importance and wide-spread occurrence. The unique property exhibited by the hydrogen atom in the formation of this bond is due to the fact that the positive hydrogen ion is a bare proton having no impeding shell of electrons around it and can attract two anions between which it forms a bridge. In the early period it was thought that the bond was symmetrical, but this has been disproved largely by the work of Pauling (107), who has also shown that one hydrogen atom can form one hydrogen bond. He stated that because a hydrogen atom has only one stable orbital, it can form only one covalent link and therefore the hydrogen bond must be due to ionic forces. The X-ray examination of compounds known to contain the hydrogen bond shows that two anions linked by a hydrogen are at a distance of 2.5 to 2.6 $\mathring{A}$, which in many cases is less than the sum of the radii of the two anions which the proton links together and much less than the sum of the radii of two atoms. Because X-rays cannot show hydrogen directly, direct proof of the hydrogen bond is difficult, but the above X-ray evidence can only be explained by putting the hydrogen between the two anions as shown in the following diagram:

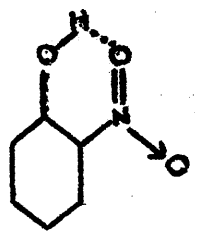


This also demonstrates how a third anion is prevented from close approach to the proton and thus the co-ordination number of hydrogen is restricted to two. Now because a proton can attract anions only, it is evident that electronegative atoms should form hydrogen bonds and that the greater the electronegativity of the bonded atoms, the greater the strength of the bond should be. Molecules or compounds containing polar groups, such as -OH , and $-NH_2$ can be linked by the hydrogen bond to each other or to other compounds containing similar groups. The hydrogen in such groups is not a bare proton. The group $-\overset{-}{O}\,\overset{+}{H}$ constitutes a dipole, and can take part in hydrogen bond formation as a proton or anion. If the resonance of the structures imparts increased electronegativity to the anions in the compound, strong hydrogen bonds can be formed, for example, in the case of phenol (108):-

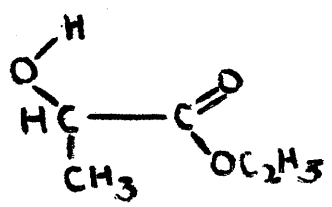


It should be realised, however, that the hydrogen is attached to one of the anions by a covalent link and linked to the other anion by the hydrogen bond as represented in, say, A–H·····B . X-ray data, however, has been very useful in measuring the distance between groups bonded by hydrogen (109). Strong hydrogen bonds are only formed if the anions concerned can approach closely enough. Thus the hydroxyl group in o-nitrophenol forms a strong hydrogen bond with the adjacent

oxygen atom of the nitro group, the O - O distance being 2.6 Å :-

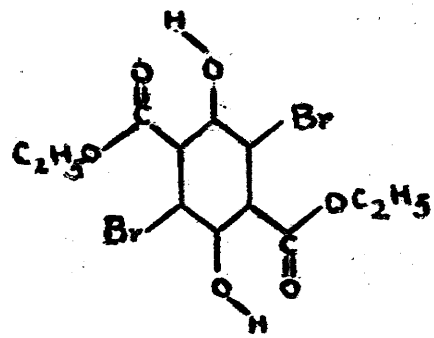


It is also necessary that the hydrogen atom should be approximately directed towards the anion which is to be bonded. The molecule should have a coplanar configuration, particularly in the case of benzene rings with attached groups, so that no steric hindrance may be offered to the approaching group in establishing contact closely enough to enable the bonding to occur. In general, formation of a six-membered ring (including the hydrogen) constitutes a favourable condition for hydrogen bonding. Ethyl lactate does not form a strong hydrogen bond, because the O - O distance is large and the



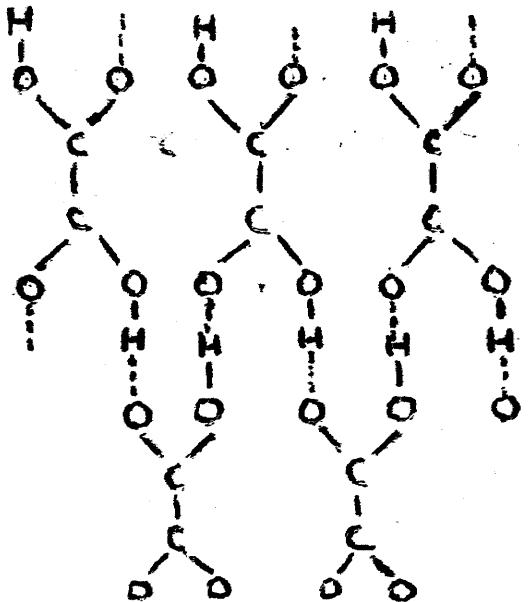
hydrogen atom of the hydroxyl group is not well directed towards the carbonyl oxygen atom. The possibility of forming a six-membered ring does not guarantee that a strong hydrogen bond

will be formed, as is seen in the case of 3:6-dibromo-2:5 dihydroxydiethyl terephthalate:-

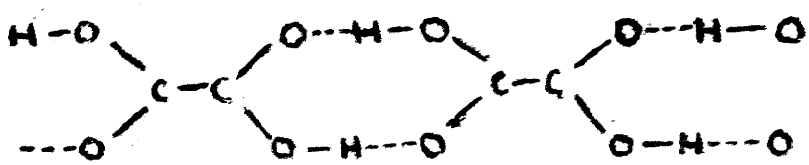


It might be expected that in this case strong hydrogen bonds will be formed between hydroxyl groups and carbonyl oxygen atoms. Infra-red absorption study shows, however, that only very weak bonds are formed. The repulsion of the bromine atoms by the ethoxy groups causes the latter to rotate about the C - C axis, resulting in an increase of the O - H ·····O distance. The fact that 2:5-dihydroxydiethyl terephthalate does contain strong hydrogen bonds supports this hypothesis of the effect of the bromine atoms (110). Further, though a conjugated system favours the formation of strong bonds, hydrogen bond formation is possible without conjugation, as just shown. Coplanar molecules can aggregate, being joined by hydrogen bonds and the crystals of such molecules exhibit certain physical properties which are the effect of the hydrogen

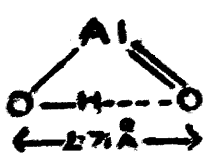
bonds. The alpha form of anhydrous oxalic acid consists of molecules joined thus to form layers:-



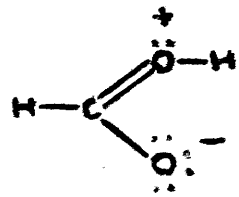
The crystal is cleaved into layers, which are joined by hydrogen bonds. The beta form consists of molecules, joined together by the hydrogen bonds into long chains thus:-



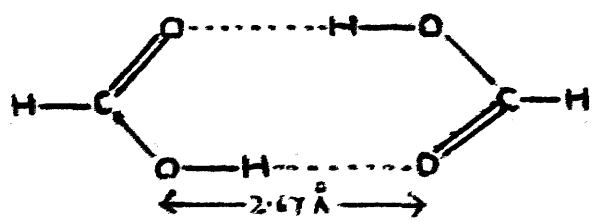
These chains are cleaved along the two planes parallel to the axis of the chains (111). Many other crystals which contain hydrogen bonds are known. Diaspore, $AlHO_2$, was investigated by Ewing (112) and found to contain a hydrogen bond, the O-H...O distance being 2.71 ± 0.05 Å. It can be represented as:-



Pauling (108) suggests that the hydrogen can be assumed to be moving in the field of a potential function with two minima situated about 1.0 Å from each of the oxygen atoms, with a to-and-fro motion, oscillating first about the one and then about the other oxygen. He states that in the O - H ·····O hydrogen bonds, the distances between anions have been generally found to be between 2.5 and 2.9 Å, wherein the equilibrium position of the proton is about 1.0 Å from one of the oxygen atoms. The resonance of the formic acid molecule:-



results in an increased positive charge on the oxygen atom which donates the proton for the hydrogen bond and a negative charge on the oxygen which accepts it. Both these effects help to increase the strength of the O - H ·····O bond in the proton. The dimer, which has been investigated by electron-diffraction (113) can be represented thus:-



The heat of association of this dimer is 14.12 K cal/mole. Therefore the energy of one hydrogen bond is 7.06 K cal./mole. In general it has been found that the energy of hydrogen bond formation lies in the region of 5-8 K cal./mole and hence the

activation energy involved in its formation or rupture is very small. It is because of this that the hydrogen bond plays an important part in reactions at ordinary temperatures.

Although the hydrogen bond is not a very strong bond, it has very important effects on the properties of substances. This has been clearly shown by the study of water molecules. It is now recognised that the high melting and boiling points and the high dielectric constant exhibited by water is due to the association of molecules by hydrogen bonds. Similar effects are also observed in other molecules in which hydrogen bonds are known to exist, for instance, ammonia and hydrogen fluoride. The hydrogen bonds in solid crystalline forms of these compounds are ruptured on fusion and yet more than half of the bonds are retained by the liquids at temperatures as high as their boiling point.

The effect on the physical properties accounted for by hydrogen bonding may thus be an indication of the formation or rupture of these bonds in molecules where such effects are observed. Conclusive evidence can only be supplied by spectroscopic study. As mentioned earlier, X-rays cannot show the hydrogen atom, due to its very small size and light weight. The characteristic frequencies of vibration of the stretchings of O - H or N - H bonds have their first overtone in the infra-red region at about 7000 cm^{-1}. Now when such groups take part in hydrogen bond formation vibration to that extent is not possible. This results in non-absorption of infra-red radiation in this region or, for that matter, in the region of

other overtones. This very important observation was made by Hilbert, Wulf, Hendricks and Liddel (110) who found that the infra-red absorption spectra of substances known to have strong hydrogen bonds within their structures does not show the presence of sharp peaks, but only diffuse bands. Since then this has been confirmed in all the substances which could be examined by this method and which are known to contain hydrogen bonds from other evidence. This vibration, it will be realised, is distinct from the oscillations of the hydfogen between two positions and it is likely that there may be strong absorption in the lower frequency regions due to this oscillation. Spectroscopic evidence, however, is not possible in many cases owing to the difficulty of finding suitable solvents for the substance under examination. It is evident that unless suitable solvent is available, the effect of solute molecules on infra-red absorption will be swamped by that of the solvent.

It will be realised that in the investigation of formation of the hydrogen bonds during attachment of, say, a dye molecule to a fibre, this method will be of no avail. The only possibility , therefore, of obtaining evidence in such cases is from physico-chemical considerations. If, for example, the energy of reaction obtained from thermodynamic calculations, lies in the region of 5-8 K cal./mole, hydrogen bonds may be implicated. Supporting evidence can also be gathered by sorption of compounds which contain internal hydrogen bonds, and thus do not have potential bond-forming groups free in the structure. However, the incomplete knowledge about surfaces and the

structure of sorbates in solution, inexact values of magnitude of energies obtained from the thermodynamic calculations, and other difficulties make it difficult to reach definite conclusions at the present moment.

PART II.

EXPERIMENTAL.

Section I. Technique and Methods.

Section II. Results and Discussion.

Section I.

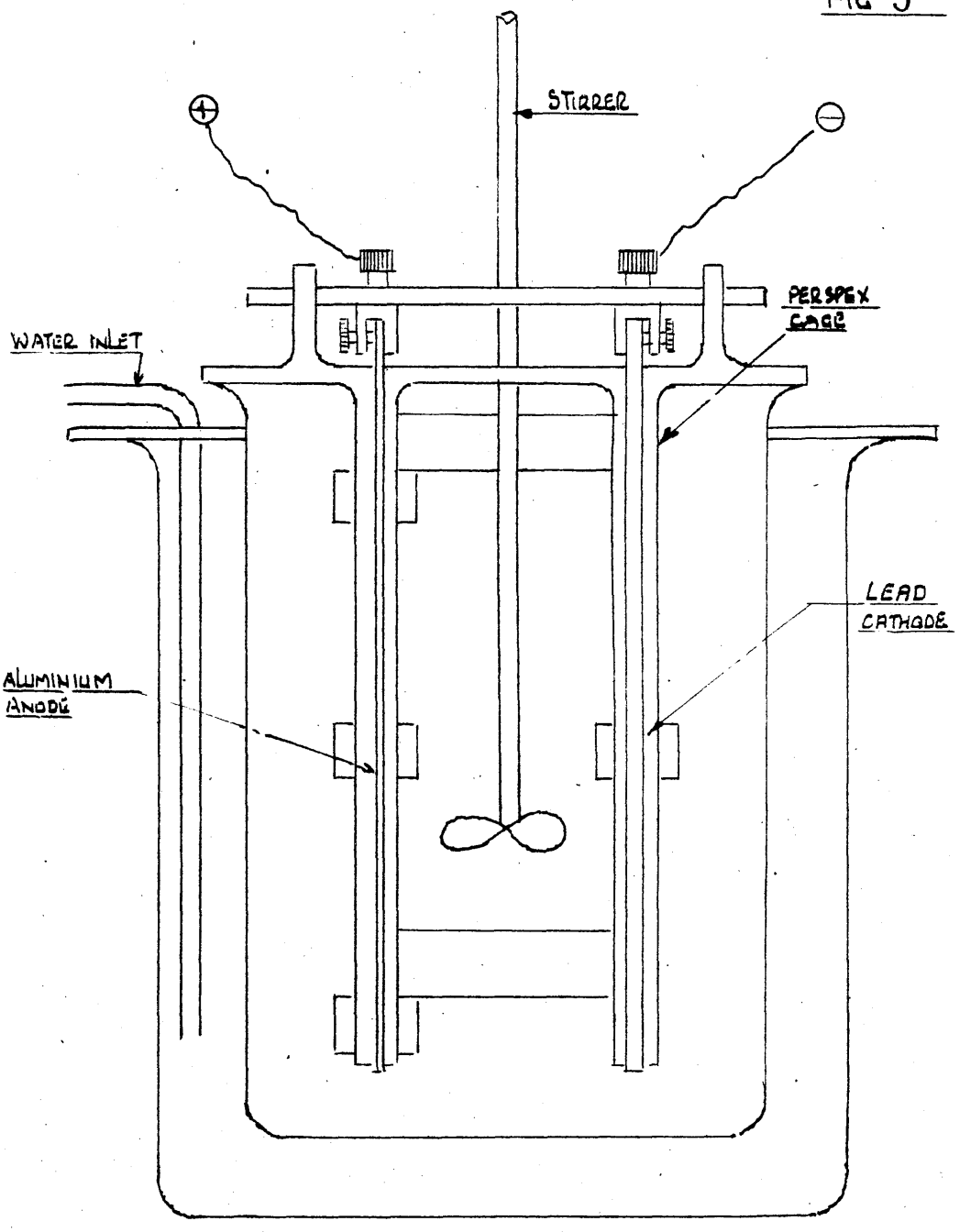
Technique and Methods.

This section will contain a description of the apparatus used and the technique and methods employed during the experimental work. The work consists of three distinct stages, anodising the aluminium foil, sorbing a substance from solution on the anodised foil and estimation of the amount sorbed. It is proposed to give general descriptions of the procedure under these heads in this section, while particular points to be noted will be included in the following section containing the results.

I. Procedure for producing anodic films on aluminium:-

(a) Anodising equipment:- This consisted of an electrolytic cell and a box containing resistances, switches etc. The cell was a 2 litre pyrex glass beaker, with a cover made from "Perspex". The cover had arms extending down into the beaker to hold in position the aluminium foil and a lead plate, which constituted the anode and cathode respectively at constant distance from each other. This beaker was surrounded by another, in which was circulated cold water to control the temperature of the anodising bath. The "Perspex" stand also held the thermometer (Figure 3). The whole apparatus was mounted on a ring burner. The leads from the anode and the cathode were connected to the terminals in the box, which supplied current from the mains. Fitted in the box was a variable resistance and a switch, which were included in the circuit (Figure 4).

FIG 3



ANODISATION CELL

The panel of the box carried an ammeter, connected in series and a voltmeter, connected in parallel.

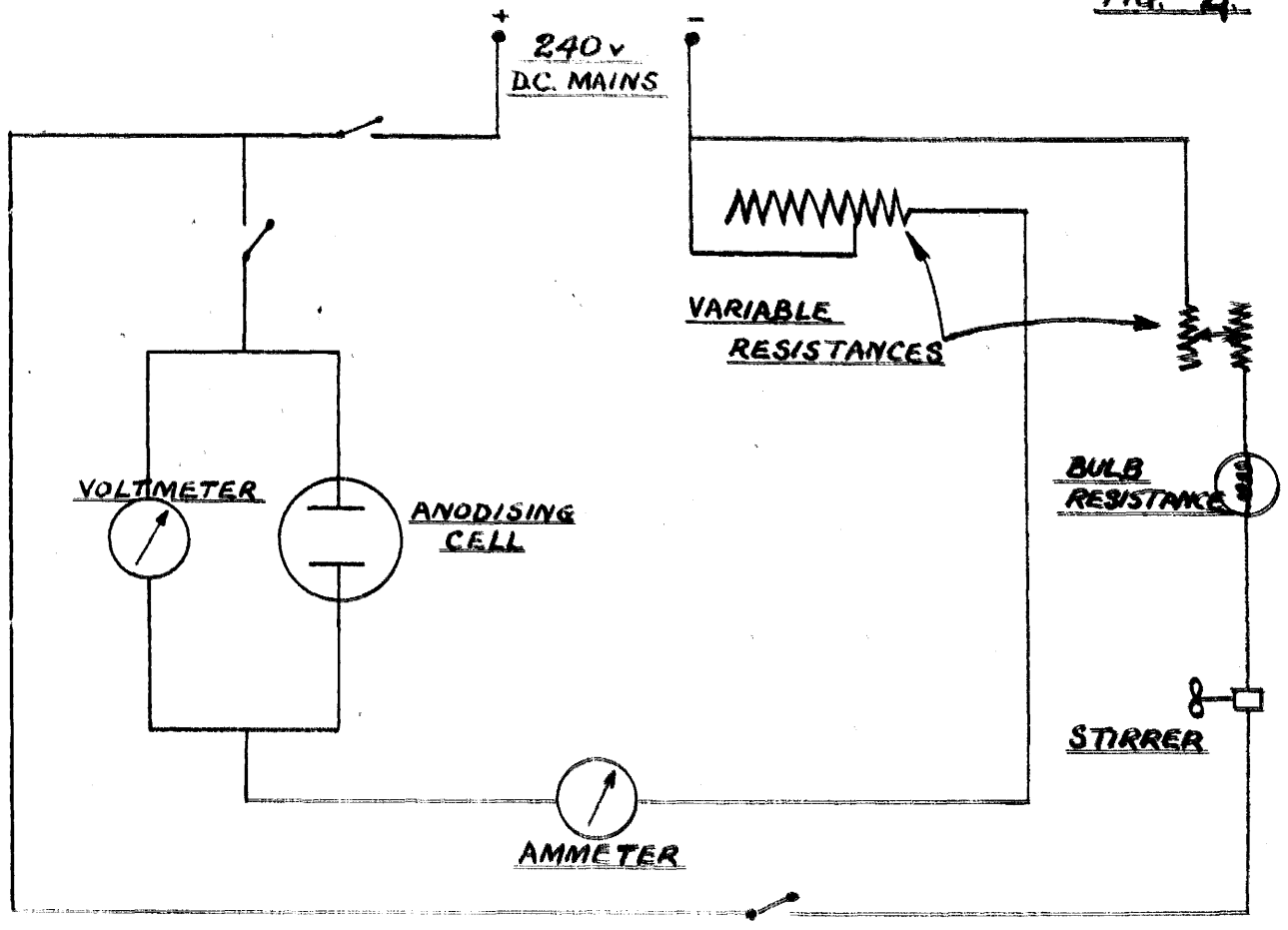
(b) Electrolytes and conditions of anodising:- In the earlier part of the work, dilute sulphuric acid, 11.0 per cent. by volume, was used as electrolyte. Initially, to determine the best conditions of anodising, a set of experiments varying the duration of anodising, the temperature of the electrolyte and the current density, were performed and the amount of film formed measured in each case. As this work does not form part of the main work and was only in the nature of preliminary trials, the results have been included in the Appendix. For the work on sorption of dyes, standard conditions of anodising the foil were used. (1 hour at 25°C. using a current density of 10 amp./sq.ft.).

Later on, chromic acid of 'Analar' quality in the form of three per cent. aqueous solution was employed as the electrolyte. The foil was anodised at 45°C. by raising the voltage of the bath from 0 to 45 in five minutes and continuing at 45 volts for fifty-five minutes, the current density then being 12 amp./sq.ft.

In view of the important effect of slight variations of conditions on the anodic film, the experimental conditions outlined above were strictly adhered to.

(c) Aluminium foil:- Pure aluminium foil (B.D.H.) was used throughout the work. The foil was anodised after cutting in suitable strips, two inches wide and about 7½ inches long, so that six 2" x 1" strips were obtained for sorption experiments.

FIG. 4.



ELECTRICAL CIRCUIT

As far as possible, for one set of experiments, strips from the same large strip were used.

Before treatment, the foil was cleaned thoroughly with carbon tetrachloride to remove grease or oil on the surface. During the process of wiping the foil dry with cotton wool, wrinkles etc. were also straightened out so that a smooth uniform surface was prepared for anodising. The foil was then washed with distilled water and screwed on as anode in the cell.

(d) Estimation of oxide on aluminium:- Of the two methods suggested by Edwards (114), that of weighing the anodised strip before and after stripping off the oxide coating was preferred because it is known to give more accurate results and is easier to carry out. He suggested that the solution should contain

Phosphoric acid (85 per cent.).....35 ml.

Chromic acid .....20 grms.

dissolved in distilled water to make a litre. In the present work the anodised strip (2" x 1") was dried in an oven and weighed after cooling in a dessicator. It was then boiled in the stripping solution for five minutes, washed, dried, cooled and re-weighed. This was repeated until constant weight was obtained. The difference in weight denoted the amount of oxide on the strip. The solution dissolved the oxide only, leaving the metal entirely unaffected.

(e) Introduction of stirrer in the cell:- When the amount of oxide formed was estimated, it was found that it varied considerably and in all the cases decreased from bottom to top of the strip. This was probably due to differences in

temperature of the bath at the top and the bottom, as a result of the anodising process being exothermic. A stirrer was, therefore, introduced in the bath to equalise the temperature. The oxide coating then formed was more uniform, as can be seen from the following table:-

Anodising Conditions	$15^{o}C.$, 1 hour, 12 Volts, 0.6amp., H_2SO_4 electrolyte 11.0%									
	Not stirred					Stirred				
	one strip		top		bottom	one strip		top		bottom
Ratio: Al_2O_3/ /Al + Al_2O_3 (%)	29.8	31.9	32.9	33.6	34.2	25.6	25.6	25.7	25.8	25.7

The resistance and a separate switch for the stirrer were inserted in the box described above. This made the equipment compact (Figure 5).

2. Sorption of dyes and other organic compounds on the anodised aluminium:-

(a) Equipment:- A rectangular copper water-bath with an aluminium cover was used. The temperature of the bath was maintained by an electric immersion heater, accurately controlled ($\pm$ $0.5^{o}C$) by a "Sun-vic" thermostatic control unit. The uniformity of temperature in the bath was maintained by circulation of water using a Stuart-Turner centrifugal pump. The aluminium cover contained round holes to hold the test tubes used as sorption baths.

Fig. 5. Anodising Apparatus.

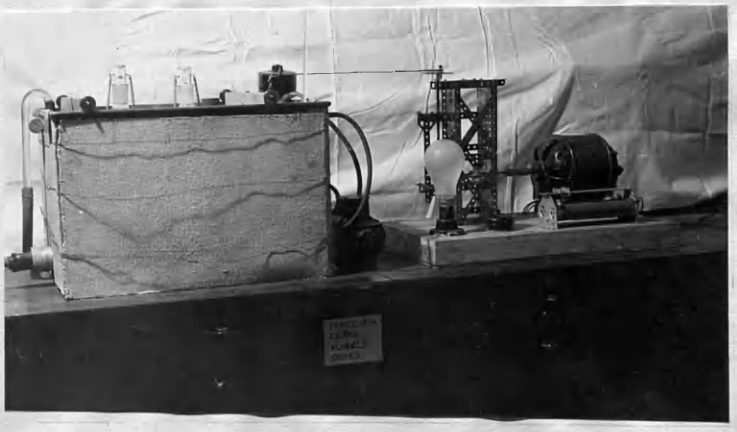


Fig. 6A. Thermostatic Waterbath
with an arrangement for agitation.

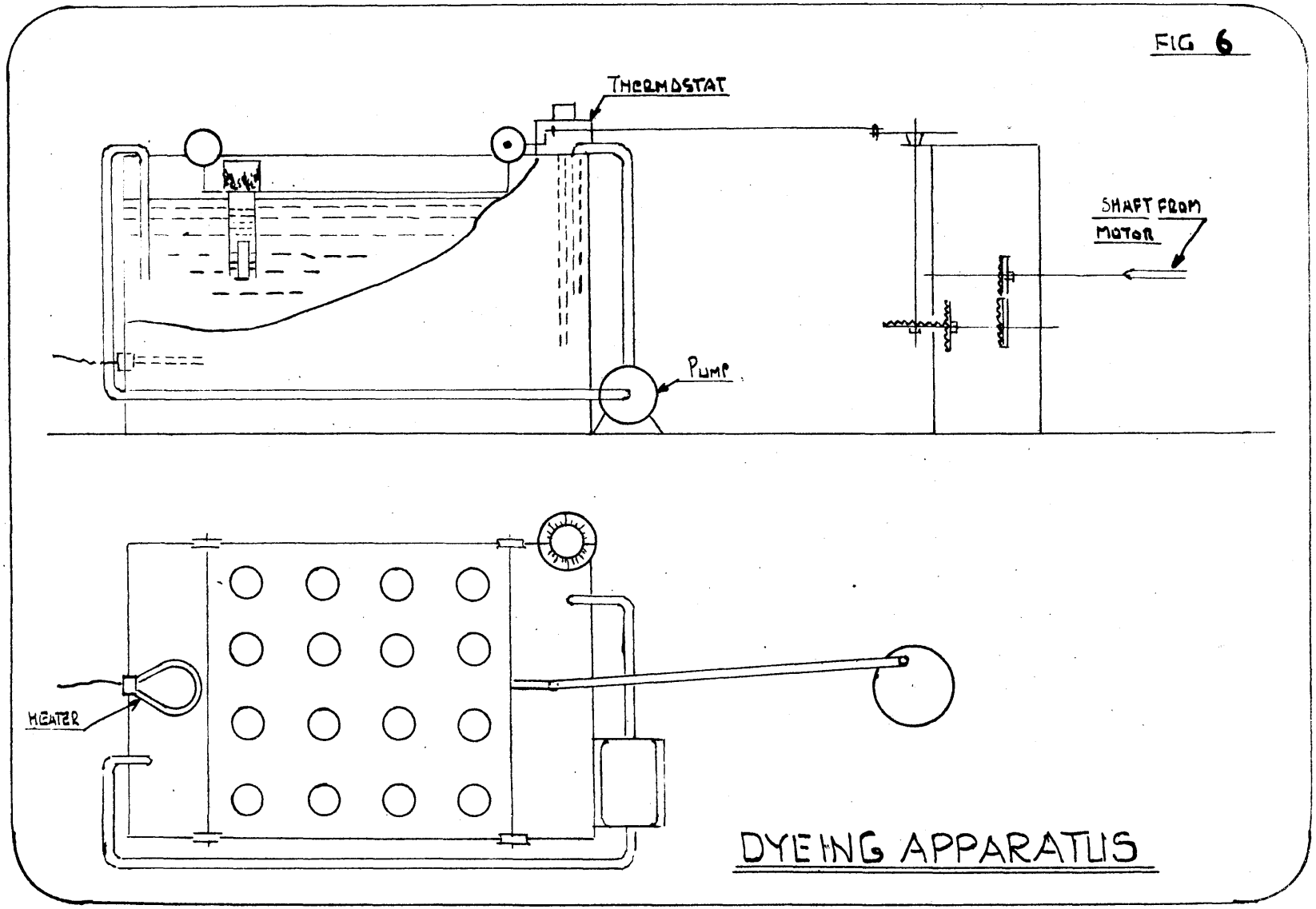
The test tubes, 8" x 1½" , were of Pyrex glass and were securely stoppered with rubber bungs for aqueous and alcohol solution; "Quickfit" test tubes with springs to hold the stoppers were used for benzene solutions.

It was observed during the sorption experiments that anodised strip took a long time, particularly at low temperatures, to reach equilibrium with the solution. It was therefore decided to agitate the sorption baths by rocking the aluminium cover holding the test tubes. This was accomplished by Meccano gearing in conjunction with a small motor (Figure 6). The equilibrium time was considerably shortened by this procedure.

(b) Dyes and other reagents used:- Special care was taken to purify the dyes used during the present work. All the dyes and other reagents employed were used in purified form. As exception was Solway Blue BNS, which could not be conveniently purified, it was used as the commercial sample. Its percentage purity, however, was determined.

Alizarin Red IP was purified by sublimation and its purity checked by melting point determination. Azo Geranine 2GS, Orange II and Orange I were each crystallised twice from alcohol-water mixture and the purity determined by means of titanous chloride. A specially pure sample of Tartrazine yellow O from the manufacturer, was used. Pure samples of benzene-azo-α-naphthol and benzene-azo-β-naphthol were used. Azobenzene was crystallised twice from alcohol and its melting point determined. All the other chemical compounds used were of 'Analar' quality.

FIG 6



DYEING APPARATUS

Aqueous solutions were made in distilled water. For non-aqueous solutions 'Analar' benzene was used after careful drying.

After the aluminium foil had been anodised it was dried in an air-oven at 110°C. for one hour and then cooled in a dessicator. A constant liquor ratio of 50 c.c. of solution for one 2" x 1" strip was used throughout. After the sorption was complete the foil was washed with the solvent several times and the washings added to the main solution. This was then made up to a suitable strength and estimated as described in the following pages.

3. Methods of estimation used:-

(a) Estimation of dyes and other coloured compounds:- The strength of the solution, if coloured, was measured on the Hilger Spekker absorptiometer. In all cases, the strength of the bath left after sorption was measured and the amount of the substance sorbed calculated therefrom. Alizarin Red IP, Azo Geranine 2G, Solway Blue BNS, Orange II, Tartrazine yellow O and Orange I were measured using visible light. Solutions of o- and p-nitrophenol, benzene-azo-α-naphthol, benzene-azo-β-naphthol, azobenzene, anthraquinone, nitrobenzene etc., were measured using ultra violet light from a mercury vapour lamp. A calibration curve for known concentrations of each compound was first obtained and the concentrations of the test solutions read from it.

Some difficulty was experienced with orange-yellow

solutions of alizarin in alcohol. The solution, it was found, was very sensitive to slight changes in p_H value. This was noted by Sörensen (115). He has even described the use of alizarin as an indicator. The addition of water to dilute the alcohol solution and different prolonged treatments during sorption changed the colour of the solution towards orange and red. It is evident that the use of the absorptiometer in these conditions will lead to unreliable results. All the solutions, therefore, were made distinctly acidic by adding one ml. of concentrated sulphuric acid (Sp.gr. 1.86) per 100 ml. of solution, before reading on the Spekker. The calibration curve was also drawn from the readings of such acidic solutions of alizarin in alcohol.

To estimate the dye sorbed on the anodised foil, it could not be removed from the foil by treatment with organic solvents, e.g. pyridine. Reagents which remove the oxide as well as the dye attack the dye and destroy it. An apparatus was, therefore, designed and constructed to measure the dye on the foil by reflection of light from it on to a photoelectric cell. A diagramatic sketch is given in Figufe 7. A parallel beam of light of constant intensity, after passing through heat and light filters, is reflected from the dyed strip and focussed on a photoelectric cell by a lens system. The energy generated thus, was measured on a moving-coil galvanometer. The reflection and hence the galvanometer reading, was expected to be proportional to the depth of dyeing of the foil. The instrument, however, did not give very accurate results, probably

because it did not possess very high sensitivity.

A very compact and well-constructed instrument known as the "Eel" reflectiometer was also tried. The results obtained with this instrument were better, but still they lacked the accuracy required for the work. Therefore throughout the work the amounts of different compounds sorbed were obtained by determining the concentration of the bath left behind after sorption and deducting it from the initial concentration.

(b) Estimation of phenol:- Phenol was estimated from the solution left behind after sorption by the bromine method. Approximately decinormal bromine solution was prepared by dissolving 2.76 grms. of potassium bromate and 15.0 grms. of potassium bromide in distilled water and diluting to one litre. This solution was standardised against decinormal sodium thiosulphate solution by adding potassium iodide and hydrochloric acid and titrating the liberated iodine in the usual manner. Ten ml. of the phenol solution to be titrated were measured out in a 500 ml. glass-stoppered bottle and 50 ml. of distilled water and 5 ml. of hydrochloric acid added to it. The standard bromine solution was added from a burette with constant shaking until a permanent yellow colour was obtained. The temperature during this addition was not allowed to exceed 20°C. by surrounding the bottle with cold water to prevent the loss of bromine. The bottle was stoppered and shaken for one minute. Ten ml. of ten per cent. potassium iodide solution and one ml. of chloroform were then added. The free iodine was titrated against decinormal sodium thiosulphate solution using

starch as indicator. From the amount of bromine solution consumed by the phenol, the amount of phenol can be calculated according to the following relationship:-

1 ml. of $\frac{N}{10}$ bromine solution $\equiv$ 0.0015675 grms. of phenol.

(c) Estimation of resorcinol and catechol:- The method of oxidation by potassium permanganate, under, first alkaline and then acid conditions, as described by Pence (116) was used for the estimation of these compounds. It is well known that acid permanganate oxidises oxalic acid to carbon dioxide and water, but alkaline permanganate, most commonly used for aromatic compounds, oxidises some of them to oxalic acid only, which can then be oxidised by acidifying the solution to carbon dioxide and water.

To perform the estimation, 25 ml. of $\frac{N}{10}$ potassium permanganate were placed in a 250 ml. Quickfit-stoppered conical flask and 2 - 3 grms. of pure sodium bicarbonate added to it; 10 ml. of the solution of resorcinol or catechol were run into the flask with gentle shaking. The mixture was boiled for about five minutes, and cooled to about $60^{\circ}C$. It was acidified with dilute (2N) sulphuric acid (25 ml.), allowed to stand for about two minutes, and cooled to room temperature. After further diluting with about 25 ml. of distilled water, 5 ml. of ten per cent. potassium iodide solution was added to it and the flask quickly stoppered. The liberated iodine was titrated with $\frac{N}{10}$ sodium thiosulphate solution, as usual, using starch as indicator.

Resorcinol or catechol is oxidised according to the

following equation:-

$$C_6H_4(OH)_2 + 13\ O = 6\ CO_2 + 3\ H_2O$$

Now, potassium permanganate, under acid conditions and, for practical calculation, under alkaline conditions as well, liberates 2.5 atoms of oxygen for each molecule, as shown in the following equation:-

$$2\ KMnO_4 = K_2O + 2\ MnO + 5\ O$$

Therefore 5.2 molecules of potassium permanganate would be required for every molecule of catechol and the factor for $\frac{N}{10}$ permanganate in terms of phenol becomes:-

1 ml. of $\frac{N}{10}$ $KMnO_4$ ≡ 0.0004231 grms. of catechol or resorcinol

According to Pence (loc.cit.), the alkaline permanganate method is applicable to single solutions of common phenols and closely related compounds such as pyrogallol, hydraquinone, etc., and is specially suitable for small quantities of such compounds.

(d) Estimation of benzene sulphonic acid and its sodium salt:-

Benzene sulphonic acid was estimated by titrating it against carbonate-free $\frac{N}{100}$ sodium hydroxide solution taking special care to prevent carbon dioxide of the air from interfering with the readings. The distilled water was boiled well before use to remove dissolved carbon dioxide and the burettes and flasks were covered with soda-lime guard tubes.

The sodium salt of benzene sulphonic acid was converted to the acid by passing the solution through a column of artificial zeolite ("H^+ cycle"). The zeolite, uniformly packed in a long separating funnel provided with a swan-neck at the exit end, was washed with boiled distilled water several times. The wash

water was slightly acidic. 100 ml. portions of the wash water were titrated against $\frac{N}{100}$ NaOH until the last two readings were of the same magnitude. This was taken as the blank reading and subtracted from the actual titre. 25 ml. solutions of the sodium salt of benzene sulphonic acid were passed through the column, follwed by 25 ml. of distilled water, three times. The whole solution was then titrated against $\frac{N}{100}$ sodium hydroxide as outlined above. This method appears to have been reported by Futterknecht (117) for the estimation of sodium sulphate in dyebaths, which is otherwise difficult to estimate. Sodium sulphate is converted into sulphuric acid by passing it through such a zeolite and is then estimated by titrating against standard alkali.

(e) Some qualitative tests:- To determine qualitatively whether some of the amines and direct dyes with diazotisable amino groups are sorbed on the anodised aluminium, diazotising and coupling on the foil was attempted. A dilute solution of Primuline in water was first tried. The dyed strip was put into a dilute solution of sodium nitrite and dilute hydrochloric acid added slowly. The strip was then placed in a dilute alkaline solution of ß-naphthol. A bright red colour was immediately developed. This showed that the amino group can be diazotised on the foil and can then be coupled with naphthol. This method, therefore, was tried for qualitative tests with aniline, p-anisidine etc.

Section II.

Results and discussion.

This section will contain details of the experimental work and the results obtained. The earlier work was done on anodic films formed in sulphuric acid electrolyte, but it was found that the results of sorption on this film were not very reliable. Further work on this type of film was, therefore, abandoned. The film formed in chromic acid electrolyte was found to be very satisfactory for sorptions of dyes and other simpler organic compounds. The detailed description of experimental work on this type of film will follow a brief report of work on sulphuric acid films. The salient features of the latter will be discussed along with the similar results of the former. The interpretation and discussion of the results will immediately follow the tabulated data.

As mentioned earlier in the introduction, the dyes used for dyeing can be very broadly divided in two categories - those which are expected to form co-ordinated complexes with alumina of the film and those which do not do this. The work will, therefore, be described under these two headings.

A. Sorption on Anodic Films formed in Sulphuric Acid Electrolyte.

(i) Dyeing with mordant dyes.

As frequently mentioned in the literature, the mordant dyes dyed the film very well and were faster than other types of dyes. It is well known that these dyes form co-ordinate complexes, some of which have a different colour from the original dye. With

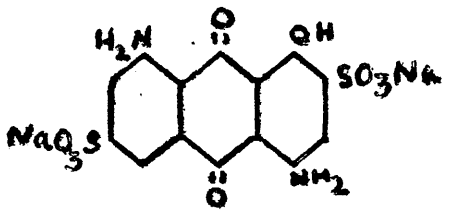
a view to obtaining some preliminary information about the behaviour of this type of dye towards anodised aluminium, qualitative dyeing experiments were carried out by applying a selection of mordant dyes to mordanted and unmordanted wool and anodised aluminium. The dyeings were then compared for shade. The following dyes were used:-

Solochrome Blue BS (I.C.I.) Solochrome cyanine RS (I.C.I.)
Alizarin Red AS (I.C.I.) Solochrome yellow 2 GNS (I.C.I.)
Solochrome Fast Orange 2 RS (I.C.I.) Brilliant Monochrome Violet 2B (L.B.H.)
Solochrome Violet RS (I.C.I.) Chrome Fast Red 2C (C.A.C.)
Solochrome Azurine BS(I.C.I.) Haematin Pure (B.D.C.)

Wool was mordanted with 3% aluminium sulphate and 3% sulphuric acid, entered cold, raised to boil within 15 minutes and boiled for 45 minutes. The mordanted and unmordanted wool was then dyed with 2% dye at the boil for 1 hour with the addition of 3% acetic acid to the dyebath. Anodised aluminium pieces were also dyed with the same percentage of dye for 1 hour at $60^{\circ}C$. On examination of the dyed woollen pieces, it was found that some of the dyes dyed the same shade on mordanted and unmordanted wool, but others gave distinctly different shades. On comparing the dyed aluminium with these dyes, it could be seen that its shade resembled the shade on mordanted wool and not that of the unmordanted wool. This showed in a qualitative manner that the dye-film combination may be of the type attributed to the dye-metal complexes formed when mordant dyes are applied to mordanted fibres.

(ii) Solway Blue BNS (Colour Index No. 1054)

The dye has the following constitution



Mol.wt. of the dye 534

Mol.wt. of dye ion 488

The commercial sample of the dye (referred to subsequently as standard dye) contained 39.5% of pure dye the remainder probably being sodium chloride. The solution prepared by dissolving 0.1 gm. of standard dye in one litre of water was used. The rate of sorption of the dye was studied by dyeing anodised aluminium pieces for different durations at four different temperatures. The results are tabulated below and plotted in Figure 7.

Table 1.

Rate of Sorption of Solway Blue BNS at 40°, 60°, 75°and 97°C.

Temp.	Amount sorbed expressed as millimoles of standard dye per Kgm. film							
	1 hr.	2 hrs.	4 hrs.	8 hrs.	12 hrs.	18 hrs.	24 hrs.	48 hrs
40°C	45.0	57.5	146.3	202.5	225.0	234.0	292.5	292.5
60°C	135.0	180.0	225.0	292.5	292.5	292.5	292.5	112.5
75 °C	45.0	90.0	180.0	180.0	292.5	292.5	225.0	112.5
97°C	180.0	202.5	90.0	85.1	57.5	225.0	112.5	180.0

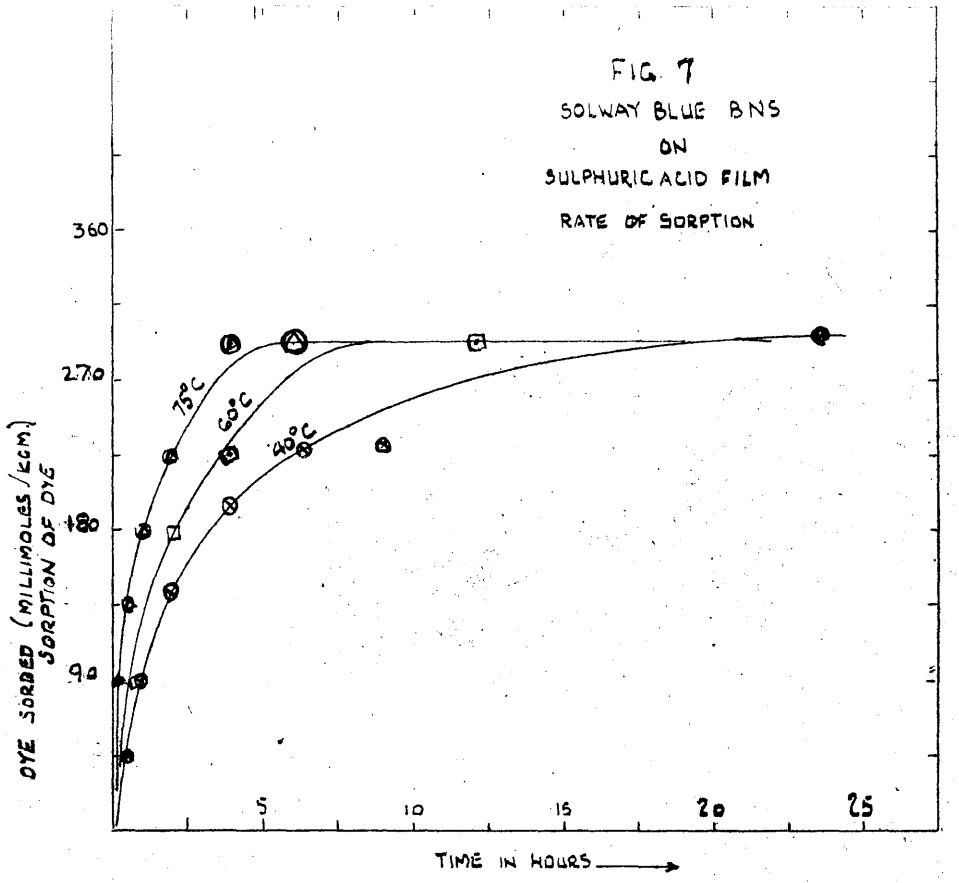


FIG. 7
SOLWAY BLUE BNS
ON
SULPHURIC ACID FILM
RATE OF SORPTION
360
270
180
90
75°C
60°C
40°C
5
10
15
20
25
DYE SORBED (MILLIMOLES/KGM.)
SORPTION OF DYE
TIME IN HOURS

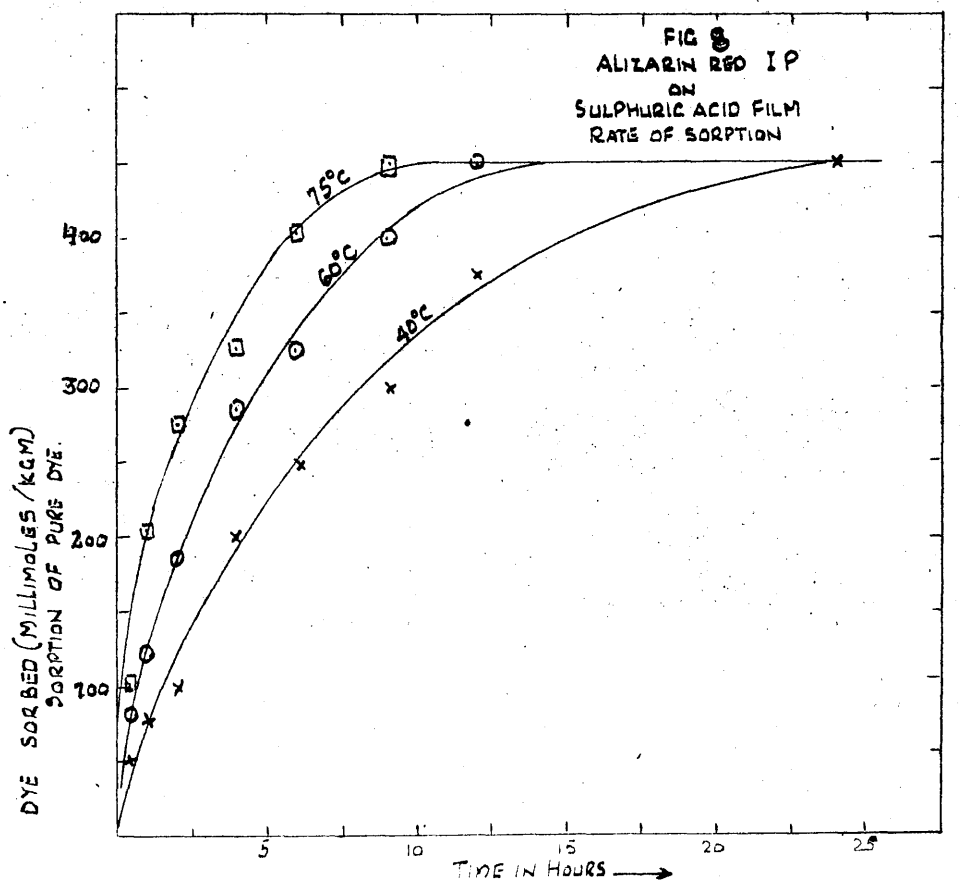
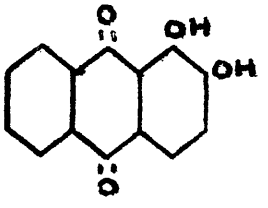


FIG 8
ALIZARIN RED I P
ON
SULPHURIC ACID FILM
RATE OF SORPTION
400
300
200
100
75°C
60°C
40°C
5
10
15
20
25
DYE SORBED (MILLIMOLES/KGM)
SORPTION OF PURE DYE.
TIME IN HOURS

(iii). Alizarin Red 1P. (Colour Index No. 1027)

The constitution of the dye is



Mol.wt.of the dye 240

The solution of the dye was prepared by dissolving 1.0 gm. of pure dye in one litre of pure ethanol. It was found that this solution did not dye the film at all, but when water was added to it, the film was dyed very deep red, which is characteristic of this dye. Five millilitres of the alcohol solution were diluted to 50 ml. with water. The dye was precipitated as a fine colloidal suspension, from which it was evenly sorbed, yielding very level dyeing. After sorption for different periods of time on an anodised piece, the dye was brought back in solution by adding more alcohol. The sorption was carried out at four temperatures, as in the last experiment. The table below contains the results obtained, which are plotted in Figure 8.

Table 2.

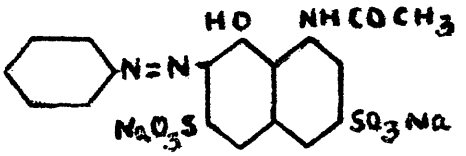
Rate of Sorption of Alizarin Red 1P at 40°, 60°, 75° and 97°C.

Temp.	Amount sorbed expressed as millimoles of pure dye per Kgm.film							
	1 hr.	2 hrs	4 hrs	8 hrs	12 hrs	18 hrs	24 hrs	48 hrs
40°C	49.6	74.4	99.2	198.4	248.0	297.6	372.0	447.4
60°C	79.2	119.0	188.4	282.4	321.0	397.0	447.0	447.0
75°C	99.2	198.4	273.0	321.0	397.0	447.0	447.0	297.6
97°C	198.4	248.0	297.6	148.8	198.4	397.0	---	---

A glance at Figures 7 and 8 at once shows that at all temperatures the maximum amount of dye going on the film is the same, indicating thereby irreversible chemical combination between the dye and the film. These results will be discussed in detail later on, when similar results on chromic acid films will be reported. It will be noticed, however, that the sorption of the dyes at very high temperatures is very erratic. The results, though expressed in tables are, therefore, not plotted. This may be due to the action of water on anodic films at high temperatures, as described earlier. At or near the boil, competition between the dye molecules and the water molecules reaches a climax. The water has the effect of "sealing" the film, probably by converting the oxide into a monohydrate which has a much lesser sorption activity. Due to this unreliability of sorption, which virtually breaks down at the high temperatures, lower temperatures were used for sorption experiments on the chromic acid films.

(iv) Azo Geranine 2G (Colour Index No. 31)

The dye has the following constitution



Mol.wt. 509

Mol.wt. of dye ion 463

The solution of the dye, prepared by dissolving 0.1 gm. of pure dye in one litre of water, was used for the experiment. The results of the sorption at four different temperatures for varying periods are tabulated in Table 3 and plotted in Figure 9.

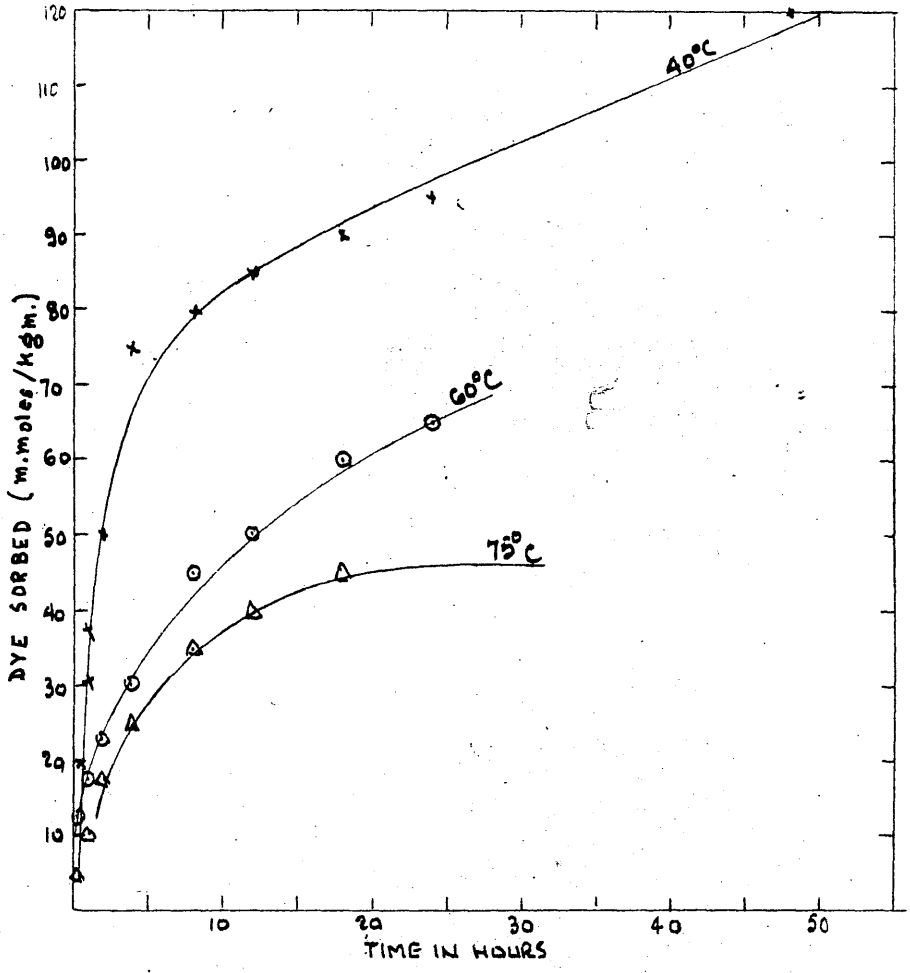


FIG 9

AZOGERANINE 2G.

ON SULPHURIC ACID FILM.

Table 3.

Rate of Sorption of Azo Geranine 2G at 40°, 60°, 75° and 97°C

Temp.	Amount sorbed expressed as millimoles of pure dye per Kgm. film.								
	½ hr.	1 hr.	2 hr.	4 hr.	8 hr.	12 hr.	18 hr.	24 hr.	48 hr.
40°C	19.6	36.3	49.4	74.2	79.6	84.1	89.2	94.3	119.3
60°C	12.0	16.9	21.8	29.3	44.2	49.5	59.6	64.3	25.1
75°C	5.0	9.8	16.9	24.3	34.2	39.4	44.1	25.6	14.8
97°C	3.4	4.9	10.1	8.7	9.3	5.7	2.3	--	--

They confirmed the doubts about the unsuitability of the film for this kind of work. In all the cases after the foil was treated with the dye solution for a time, it appeared as if the dye was coming off the film because the dyebath concentration as estimated on the Spekker registered a rise. Now, this may be due to several reasons. Two of these are most likely. The dye in solution on prolonged treatment may suffer from "ageing". That this is possible is shown by the work of Lenher and Smith, (122), who observed that a solution of dye increased in particle size by 30% on ageing for several days, and by almost 100% after a month. They have not explained this but it would appear to be a typical case of slow coagulation. The other reason may be the impurity of the sulphuric acid film. It is now agreed that this film contains about 13% aluminium sulphate, probably as a basic compound. Though it is mentioned that this basic sulphate is firmly anchored in the film, some of it may come down in the bath at the temperatures at which the film is treated

with dye solutions especially after prolonged periods. This would then increase the optical density of the dye solution, and also help the slow coagulation process mentioned above. Pullen (3) confirmed this, and recommended the use of chromic acid film as being better for sorption work. These findings have no bearing on commercial practice, where probably sulphuric acid films may be found to be better from many points of view. The advantages of this anodising process have been outlined in the introduction and need not be repeated here. It is thought very likely that the findings upon the mechanism of sorption on chromic acid films would apply equally well to sulphuric acid films.

B. Sorption on Anodic Films formed in Chromic Acid Electrolyte.

Chromic acid film is known to contain almost pure aluminium oxide containing only traces of chromium (31). The advantages of a substrate in a pure state for sorption work are evident.

The sorption of dyes and simpler organic compounds was carried out on this film. The dyes were of two types - lake-forming and ordinary acid azo dyes. In order to understand the behaviour of these dyes towards the film, simple organic compounds like phenols, benzene sulphonic acid etc., were selected for sorption. This will be described after the work on dyes of the acid azo class. The methods of estimation of these compounds have been described in the earlier section.

Lake-Forming Dyes.

(i) Solway Blue BNS:-

The sorption of this dye was studied in the same way as in the case of sulphuric acid film at 25°, 40°, and 60°. The results so obtained are contained in Table 4 and plotted in Figure 10.

Table 4.

Rate of Sorption of Solway Blue BNS at 25°, 40°, and 60°C.

Temp.	Amount sorbed expressed as millimoles of std. dye per Kgm.film.							
	2 hr.	4 hr.	8 hr.	16 hr.	24 hr.	48 hr.	96 hr.	144 hr.
25°C	32.2	67.4	76.7	94.5	112.1	144.2	180.0	212.3
40°C	40.5	64.4	--	85.2	110.2	181.3	--	212.3
60°C	78.8	89.8	89.8	150.5	164.1	212.3	212.3	---

(ii) Alizarin Red 1P:-

It was observed in this case also that no sorption of dye took place from the pure alcoholic solution. The dye solution was, therefore, diluted 10 times (5 ml. dye solution to 50 ml.) with water. The temperatures of sorption used were, 25°, 40°, 60° and 80°C. The dye left in the bath was estimated as stated before. Table 5 contains the results of the sorption tests and the curves of rate of sorption are plotted in Figure 11.

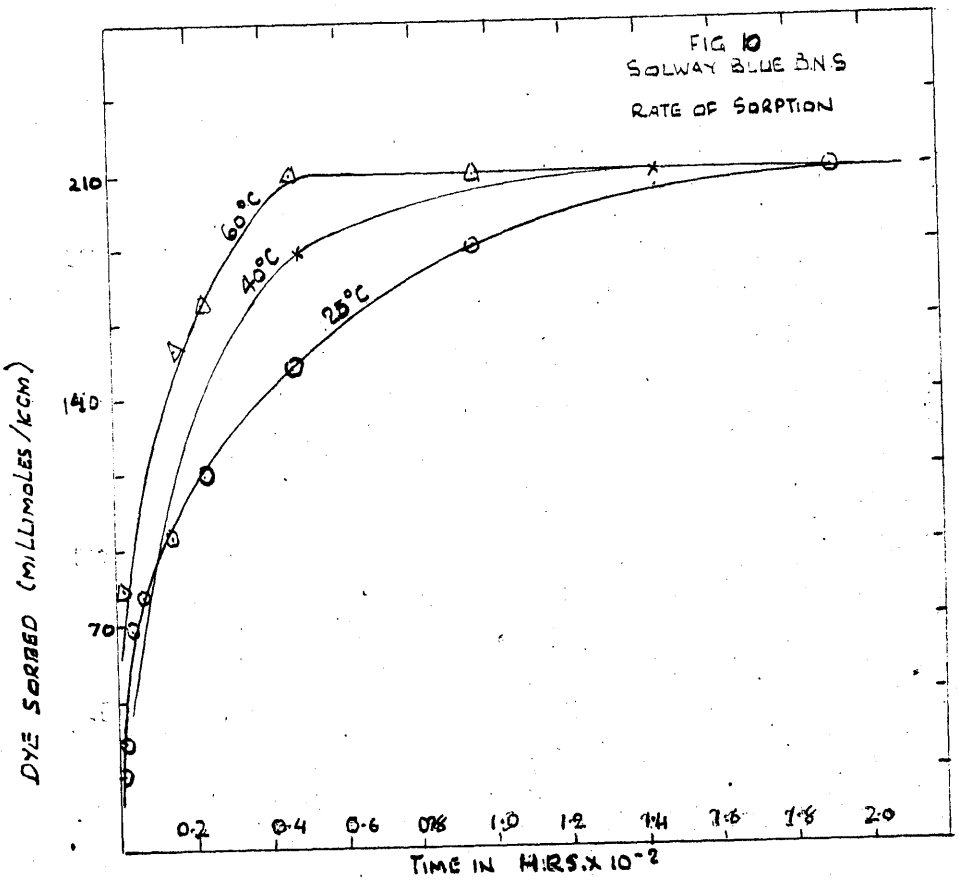


FIG 10
SOLWAY BLUE B.N.S
RATE OF SORPTION
DYE SORBED (MILLIMOLES/KGM)
210
140
70
60°C
40°C
25°C
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
TIME IN HRS. X 10⁻²

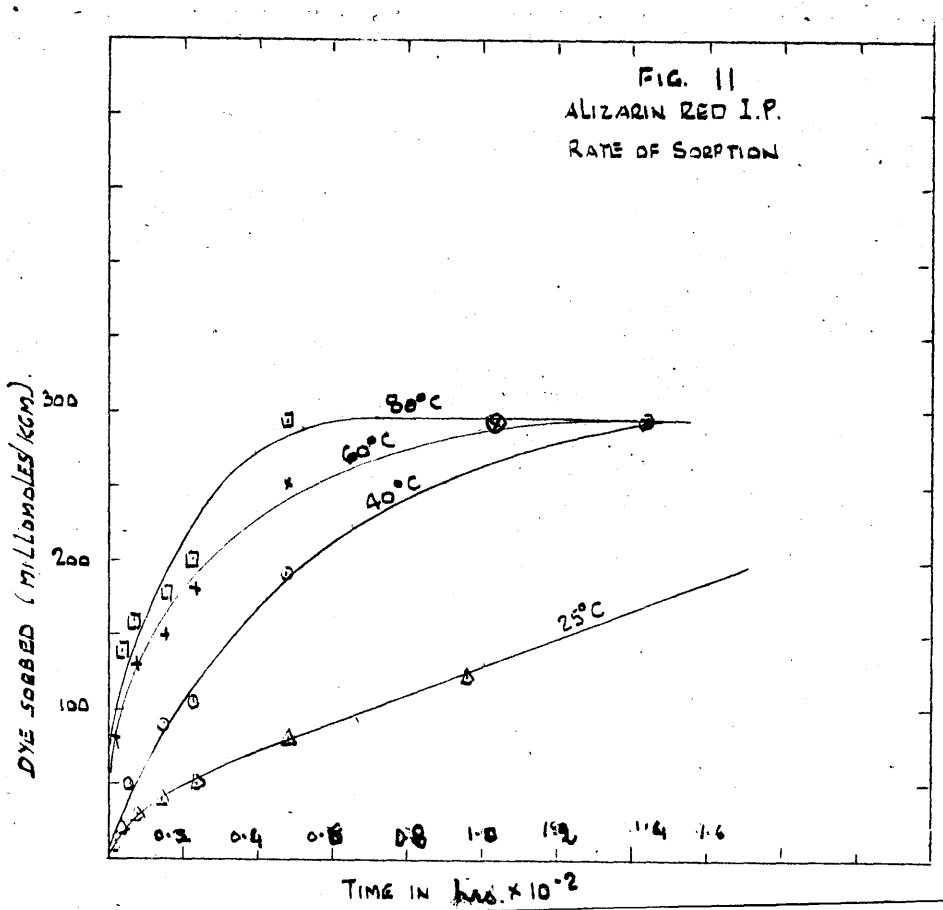


FIG. 11
ALIZARIN RED I.P.
RATE OF SORPTION
DYE SORBED (MILLIMOLES/KGM)
300
200
100
80°C
60°C
40°C
25°C
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
TIME IN hrs. X 10⁻²

Table 5.

Rate of Sorption of Alizarin Red 1P at 25°, 40°, 60° and 80°C.

Temp.	Amount sorbed expressed as millimoles of pure dye per Kgm. film.							
	2 hr.	4 hr.	8 hr.	16 hr.	24 hr.	48 hr.	96 hr.	144 hr.
25°C	9.92	19.9	29.8	39.7	49.6	80.9	119.2	--
40 °C	19.9	49.6	--	80.2	99.2	178.6	289.0	289.0
60°C	80.0	99.2	129.0	148.7	178.6	255.0	289.0	289.0
80°C	85.7	138.8	158.7	174.6	196.7	289.0	--	--

As observed in the case of sulphuric acid film, the figures 10 and 11 show that in this case also the equilibrium sorption of each dye at four different temperatures is the same. It is interesting to note, however, that though the average amount of film both in the case of sulphuric acid film and chromic acid film was approximately the same (21 mgms. per sq.inch), the sulphuric acid film sorbs more dye than the chromic acid one. It is quite reasonable to assume that the forces of sorption playing a part in both cases are the same. The larger sorption on sulphuric acid film may, then, be due to the more porous nature of the film so that dye molecules are able to penetrate to a greater depth. The pores of the film are conical in shape and the diameter of the pores is so small at the film-metal interface that the whole cross-section of the film is never dyed (3). It may also be due to the presence of basic sulphates in the film.

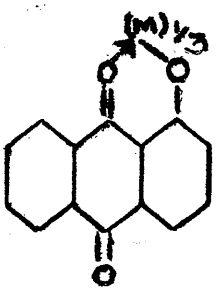
A dyeing process could be divided into two stages, viz., the approach of the dye molecules or ions to the sites in the film,

and their fixation. It is well known that aluminium oxide in water possesses a positive charge. Assuming that the film also has a positive zeta potential (this will be considered in greater detail later, when reasons to substantiate the assumption will be given), it will attract negatively charged dye ions in solution. Once the dye ions are brought near the sites of sorption under the influence of electrostatic forces, the ions are adsorbed first. That this is so is indicated by the nature of the curves. The shape of the curves resembles that of adsorption curves in general. Again, the higher the temperature, the higher is the rate of sorption, which is a characteristic of adsorption processes. Ultimately, of course, chemisorption takes place.

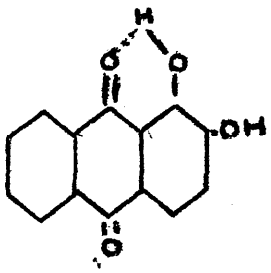
Different views about lake-formation held, by different schools, have been mentioned in some detail in the earlier section. Thus, Weiser et al (101) believe that lake-formation is a mere adsorption process. Morgan and Drew and their collaborators have proved quite conclusively that the lakes are co-ordinate complexes with a chelated metal atom. The fastness of these dyeings on anodised aluminium compared with other acid dyes and the constancy of the amount of dye combining with the film are indicative of the complex formation foreshadowed by the Morgan school. It is suggested that both adsorption and chemical combination are taking place. Giles (123), in an excellent survey of the information on the mordanting of animal fibres, suggests similarly that the process of mordanting may be regarded as occurring in two stages - the initial stage of diffusion and

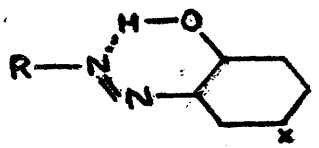
physical adsorption, to be followed by fixation of the mordant by chemical forces.

Werner (96), in his co-ordination theory, showed that a central atom could be attached to a definite number of other atoms or groups by co-ordinate links. This maximum number of other atoms or groups he called the co-ordination number of the central atom. Sidgwick (124), giving an electronic interpretation of Werner's theory, showed that the co-ordinate links of Werner were really covalent links, and the co-ordination number was the maximum covalency number. According to Sidgwick's covalency rule (125), elements may have a maximum covalency of four, six or eight (except hydrogen, which has a maximum covalency of two). Extending the ideas of Werner, Morgan et al explained the formation of chelate compounds of dyes of the alizarin type with metals like cobalt and aluminium. In elucidating the constitution of these metal complexes, they showed that the metal atom exhibited its maximum covalency. Sidgwick (126) distinguishes these chelate rings from the ordinary isocyclic and heterocyclic rings of organic chemistry as having co-ordinate links. Hence, a tervalent metal atom like aluminium, for example, will exhibit three covalencies and three co-ordinate valencies, the latter being usually shown by an arrow:-



It has been shown by Flett (127) that the 1-hydroxyl group of alizarin takes part in the formation of a six-membered ring by hydrogen bonds to the adjacent carbonyl oxygen, while the 2-hydroxyl group is a free group, thus giving rise to a characteristic infra-red absorption band. Similarly, in the ortho-hydroxyazo compounds, a hydrogen-bond structure through a N·····H - O link exists:-





Hunter and his collaborators (128) have shown that by replacing hydrogen by metal in the ring, chelate metallic compounds could be obtained. This disproves the structure proposed by workers from the Italian school (129) in which they retained the hydrogen atom in the structure.

We shall accept the view that a hydrogen atom is replaced when a chelate compound is formed. Then three alizarin molecules will attach themselves round a central aluminium metal atom. According to Sidgwick's covalency rule, the alizarin molecules will be attached by six links to the aluminium atom, each alizarin molecule being linked at two points. Although Sidgwick distinguishes a co-ordinate link as a source of instability as compared with a covalent link, it should be difficult to distinguish them, as all the six covalencies according to the covalency rule, share between them twelve electrons.

To understand the rules of covalency, let us examine the electronic configurations of atoms in their normal states. These consist of shells made up of varying numbers of orbits, which are occupied by electrons. One atomic orbital can be occupied by one electron or two electrons with opposite spins. The first shell, K, has 1s orbit which can be occupied by two electrons with opposed spins to complete it, as is the case with helium. The next shell is the L shell, composed of four orbitals, 2s, $2p_x$, $2p_y$ and $2p_z$, of which 2s is somewhat more stable than $2p_s$. Electrons first occupy the stable orbital doubly, and then equally distribute amongst other orbitals of the same energy level, maintaining their spins parallel. The next is the M shell with 9 orbitals; and so on. Thus, if the quantum number of the shell is n , there are n^2 orbitals and $2n^2$ electrons occupying completed shells. The approximate relative energy values for atomic orbitals are indicated in Figure 12.

The complex quantum mechanical treatment of valency stated simply would mean that an atom can form a covalent bond for each stable orbital and therefore such a bond would need two electrons with opposite spins and a stable orbital of each of the two atoms to be joined. Among the electrons of an atom, it is better to distinguish between those of the core or inner stable orbitals of unshared electrons which do not take part in chemical combination and those of the valency group consisting of shared electrons and any unshared ones which are not accommodated in the inner shell. It has also been shown by quantum-mechanical treatment that in general formation of a covalent bond stabilises a molecule so that the most stable electronic configurations will

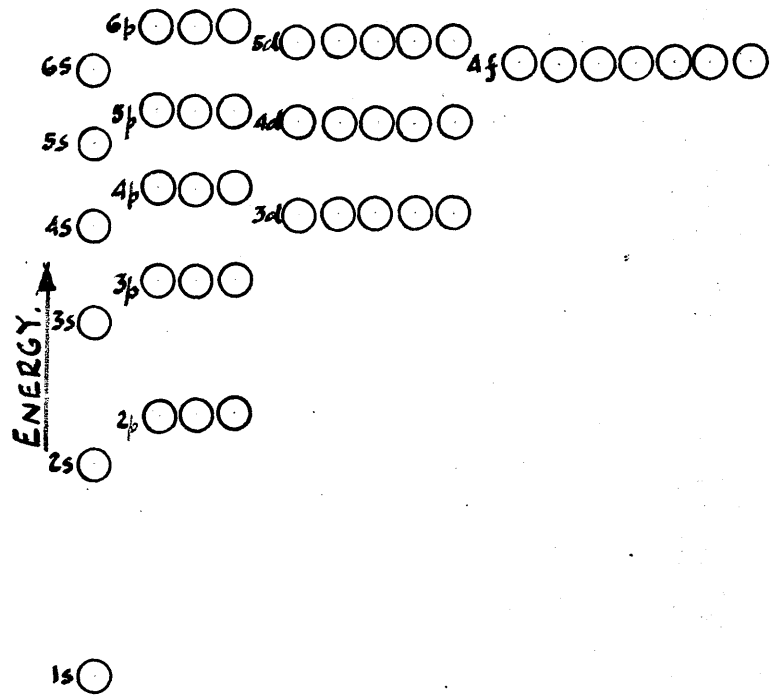


FIG. 12.

APPROXIMATE RELATIVE ENERGY SEQUENCE OF ATOMIC ORBITALS.(108)

be those in which all the stable orbitals of each atom are used either in bond formation or occupied by an unshared pair of electrons. Accordingly a maximum of nine covalent bonds should theoretically be formed by atoms from sodium to chlorine in the Periodic Table, but this is not known to happen. There are many other limitations which restrict the number of atoms that can be bonded to a central atom.

Now we shall examine aluminium from the point of view of these facts. The aluminium atom has the following electronic configuration

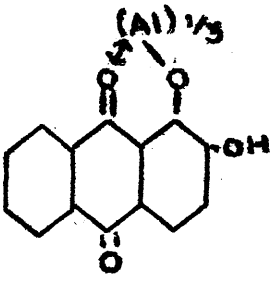
	K	L		M		
	1s	2s	2p	3s	3p	3d
Al 13	2	2	6	2	1	

K and L shell electrons form the core or inner group of unshared electrons while three electrons in the M shell constitute a valence shell. Figure 12 shows that 3d orbitals have a higher energy level, and hence lesser stability, than the 3s and 3p orbitals. They are four in number and hence it is suggested that probably the aluminium atom has an ordinary maximum covalency of four in its normal state. The use of 3d orbitals should not be completely ruled out but owing to its comparative instability it is likely that normally four stable orbitals (one 3s and three $3p_s$) take part in bond formation, although the compounds of the type $Na_3[AlF_6]$ may be formed by some of the 3d orbitals taking part in bond formation. If we suppose that normally an aluminium atom exhibits a maximum of four covalencies three of them can be satisfied by three

alizarin molecules (aluminium being a tervalent element) and the fourth perhaps by a water molecule. Many examples are known where water molecules are attached to the central atom by covalent bonds, the oxygen atom donating the electrons. This may be the reason why water is necessary in the dyebath to form dye-metal complexes and thus satisfy all the covalencies of the metal atom.

This structure will not explain the stability of the complex It is suggested that the electrostatic attraction between the metal atom and the carbonyl oxygen results in a bond. Formation of three such bonds gives stability to the whole complex. One covalent bond and one electrostatic bond help to constitute a chelate ring. Langmuir (130) has shown that electrostatic forces could interact to form a bond which is known as an "ion-dipole" bond. The presence of a hydroxyl group in the 2-position increases the negativity of the molecule, thus facilitating the formation of the electrostatic bond. This may be the reason why 1-hydroxyanthraquinone does not form a chelate compound. If we accept Sidgwick's conception of chelation (126, p.231) it is difficult to explain why this compound is not a useful dye. Though Morgan and Main Smith (131) state that in the alizarin series, this compound is not sufficiently acidic and hence to produce a stable lake, the acidity of the molecule should be increased by introducing an acidic group in the 2-position in order to distinguish this type of bond from others, it is suggested that a red arrow with heads at both the ends may be used to denote mutual attraction between the atoms. The complex may,

therefore, be represented as:-



This would indicate that the central aluminium atom has seven links round it which may still be called its co-ordination number. It should be noted that this is different from its maximum covalence. Pauling (108, footnote p.32) also regards this distinction as necessary and to quote his words "a sharp distinction is to be made between the number of atoms bonded to a central atom (the co-ordination number of the central atom) and the number of covalent bonds formed by the central atom (its covalence). These numbers may, and often do, differ, as a result of the attachment of some of the surrounding atoms by bonds of type other than single covalent bonds, such as double bonds or electrostatic bonds."

A comparison of the combining capacity of the two dyes and the two films should be interesting. Table 6 shows the proportion of pure dye expressed in gm.-moles per mole of the oxide of the film.

Table 6.

Comparative combining capacity of the dyes.

Type of film	Amount combined in gm. moles per mole of oxide		
	Alizarin	Solway Blue BNS	Ratio
Sulphuric Acid	.045	.013	3.46
Chromic Acid	.029	.009	3.22

It will be seen that no definite proportion between oxide and dye exists in either film. This can be understood when it is realised that only a part of the film is dyed at saturation. Alizarin combines more than Solway Blue BNS. It is evident that the size and shape of the molecule should play an important rôle in dyeing of the film, and hence, other conditions being the same, the smaller molecule without any groups offering obstruction to its passage through the pores should be sorbed more. Electrical factors may also play a part. Solway Blue BNS has two sulphonic groups in its molecule, which should give it an added charge . The attraction between the positively charged oxide of the film and the negatively charged dye ion will not allow the dye ion to diffuse inside the pores smoothly. This electrostatic resistance may result in a lower equilibrium sorption. It is difficult to judge the effect of these factors but it is quite likely that all of them have some effect. It is probably because of this that varying proportions of oxide will be effectively taking part in sorption of dyes and other compounds. As the extent of this effect of these factors is difficult to judge, it is not

possible to draw any conclusions as regards the combining proportions of the dye and the film. It is therefore equally difficult to forecast the sorption of new dyes on knowledge gained from other dyes. It is, however, interesting to note that sulphuric acid film sorbs more dye than chromic acid film, probably for reasons stated before and the ratio of Alizarin sorbed on both the films is approximately equal to the ratio of Solway Blue BNS on them. This probably indicates that the factors affecting sorption of these dyes on one film are also proportionally playing their part in sorption of the same dyes on the other film.

Acid Dyes.

A systematic investigation into the mechanism of sorption can be divided into two sections, based on a kinetic and a thermodynamic treatment, respectively. The work on rates of sorption constitutes the former, and sorptions at equilibrium, the latter. While the study of kinetics helps to elucidate the way in which a substance is transferred from the solution to the film and the speed at which this occurs, it is the thermodynamics approach which gives an insight into the mode of attachment of molecules of the substance to molecules in the film.

The work on the rate of sorption of dyes showed that they were sorbed by the anodic film very slowly at lower temperatures, though, of course, the velocity increased considerably at higher temperatures. Pullen (3) indicated that sorption of dyes on the film is very rapid and it appeared in practice that no more dye was sorbed after a few minutes. It is well known that stirring of the bath considerably quickens the speed of sorption and in the present work it was found that by introduction of agitation of the bath, and higher temperatures, which are the conditions generally used in practice, most of the dye was sorbed within a few minutes. However, it will be realised that in work of this nature, the experiments should be carried out until equilibria have been attained with certainty. Hence, even though in many cases it will be found that periods of sorption are much longer that usual in practice, the information derived from this study by applying the principles of kinetics and thermodynamics is not only a matter of theoretical importance but can have a bearing on

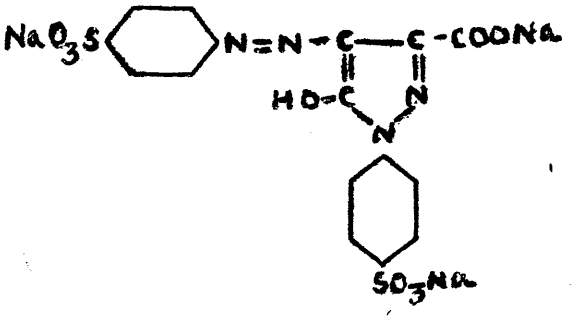
practice. Practical aspects of this study will be discussed at the end of this section.

Study of the rate of sorption of Tartrazine O was first taken up, but later on it was thought that by selecting simpler dyes like Orange I, complications arising due to complex structure may be avoided, and perhaps it may be easier to find reasons for various experimental observations. Rates of sorption of Orange I, Orange II and Azo Geranine 2G were determined and interpreted in some detail. The equilibrium sorptions of the same dyes were also studied and interpreted so as to obtain some idea of the affinities of the dyes for the film and the nature of the linkage involved.

1. The Kinetics of Sorption.

(i) The Rate of Sorption of Tartrazine O (Colour Index No.640)

The dye has the following constitution



Mol.wt.of dye 534
Mol.wt.of dye ion 465

A specially pure sample of the dye, supplied by the manufacturer, was used to make a 0.1 gm. per litre solution. The rates of sorption of the dye on anodic film were determined by dyeing it for various durations from a bath of 50 ml. of dye solution at 25°, 40°, 60° and 80°C . The results so obtained are contained in Table 7 and plotted in Figure 13.

Table 7.

Rate of Sorption of Tartrazine O at 25°, 40°, 60° and 80°C .

Temp.	Amount sorbed expressed as millimoles per Kgm. dry film						
	2 hrs.	4 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	144 hrs.
25°C	18.05	40.50	58.55	68.00	71.00	74.75	96.75
40°C	24.75	27.25	30.35	31.55	36.00	38.25	42.75
60°C	11.25	14.25	19.10	25.95	27.15	28.20	31.55
80°C	11.25	15.75	18.05	20.25	22.50	22.50	---

It should be noted that these rates were determined without continuous agitation of the dyebath and hence they are very slow. Sorption goes on for more than six days; and though at higher temperatures it is getting slower as the time is prolonged, curves indicate that at 25°C. there is no sign of reaching equilibrium

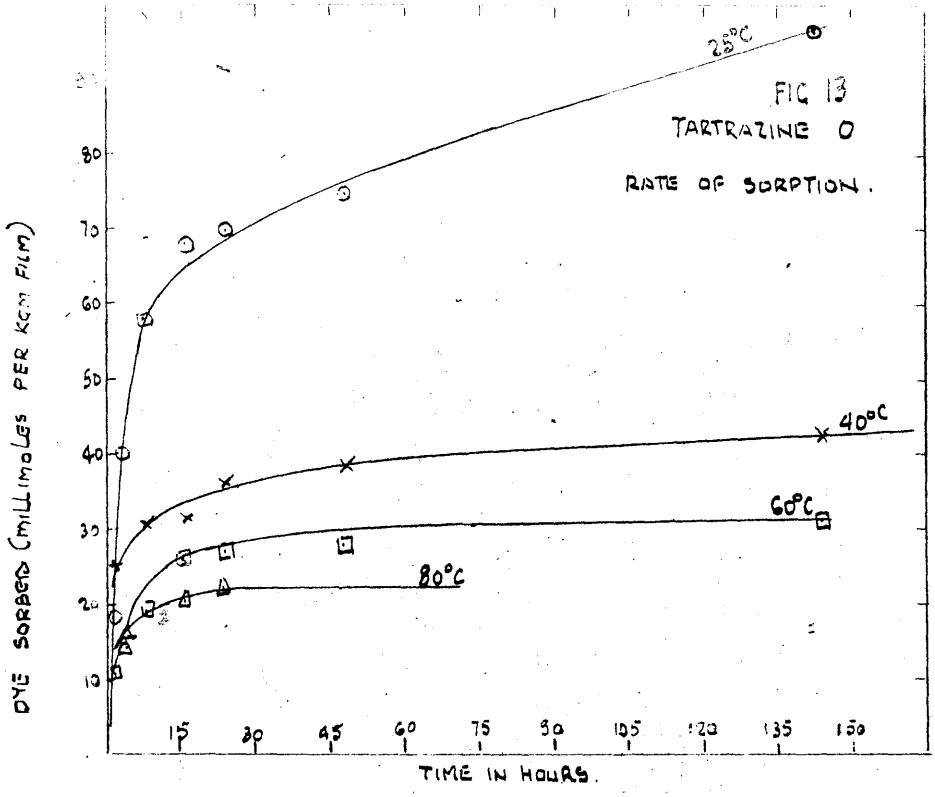


FIG 13
TARTRAZINE O
RATE OF SORPTION.
25°C
40°C
60°C
80°C
DYE SORBED (MILLIMOLES PER KGM FILM)
TIME IN HOURS.

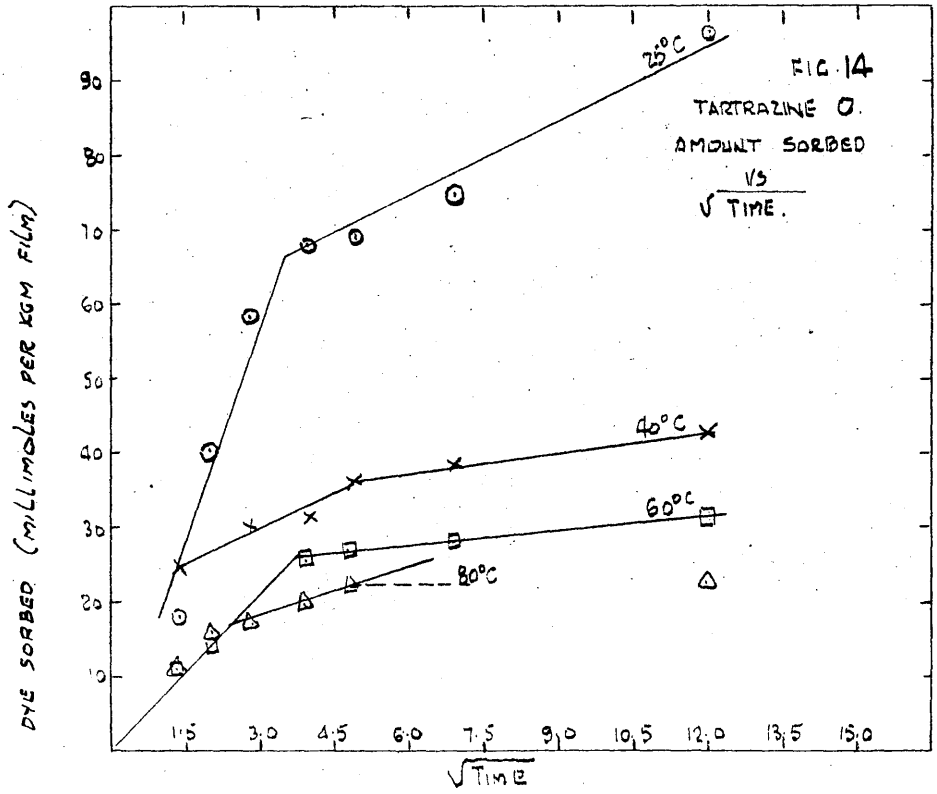


FIG. 14
TARTRAZINE O.
AMOUNT SORBED
VS
√TIME.
25°C
40°C
60°C
80°C
DYE SORBED (MILLIMOLES PER KGM FILM)
√TIME

even after six days. The velocity of reaction at 40°C. is higher than at 25°C. but at 60°C. and 80°C., it drops. It is difficult to explain this. It may be due to increasing solubility of the dye in water at higher temperature. It is evident that sorption of dye on the film is a net result of attraction of the dye for water and for the film. If the temperature has considerable influence over solubility of the dye in water, it will adversely affect the attraction of the dye for the film. A large drop in sorption of Tartrazine O at 40°C. from that at 25°C., at or near equilibrium points to the same explanation.

It is, however, interesting to note that the curves show a regularity with respect to effect of temperature on sorption at or near the equilibrium; the higher the temperature, the lower is the amount sorbed. This indicates that the same forces of attraction are at work in all cases. These may be considered as adsorption or diffusion forces.

Fick's Law of Diffusion has been stated earlier (p.39). According to this, if the sorption is governed by diffusion, the plot of amount sorbed against the square root of time should be a straight line at least in the initial period. Later on, when absorption occurs during a diffusion process, the slope of the line falls off because the apparent diffusion constant is smaller than the "true" diffusion constant of the substance (56). The rate-data of Tartrazine O have been plotted in Figure 14. to test the application of the simple diffusion theory. Instead of one line, two straight lines are obtained for each temperature*.

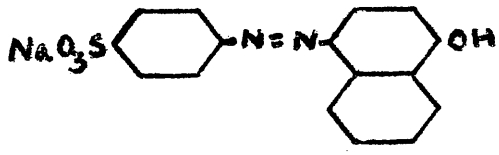
*(It may also be possible to draw a curve through each set of points).

The first line indicates the diffusion of dye in the earlier stage, the second line may be due to sorption occurring within the pores of the film as mentioned above. It is unlikely, however, that the process of diffusion coupled with sorption would give a straight line as it does in the second stage. It is suggested therefore that the film may have more than one layer, and each line represents diffusion in a different layer. Pullen (3) has indicated that this is likely. The film is known to have pores of conical shape, with decreasing diameter towards the interior. The diffusion theory envisages that within reasonable limits the dimensions of the capillary canals through which a substance diffuses will remain uniform. When the diameter of the pores diminishes then one set of conditions that have governed the process has now become changed, and thus the value of the constant should change, so as to be applicable to the new set of conditions. As, now, greater resistance will be offered to the passage of the dye molecules within the pores, the diffusion constant should have a smaller value. Hence if it is still a diffusion process, the plot should be a straight line with a lower value of the slope. This may amount to saying that the film is built up of layers. The curves in Figure 14 indicate such a possibility, though it is difficult, however, to say this with certainty because the number of points on each section of the curve for each temperature is insufficient. The curves should originate from the zero point. This is the case in the curves for temperatures of 25°, 60°, and 80°C., but that for 40°C. does not pass through the origin. We do not know the

reason for this anomaly.

(ii) The Rate of Sorption of Orange I. (Colour Index No.150)

The dye has the following constitution



Mol.wt.of dye 350

Mol.wt.of dye ion 327

Solution of pure dye of concentration 1.0 gm. per litre was prepared. For rate work, this solution was diluted to the concentration of 0.1 gm. per litre, and as in previous cases 50 ml. of this solution was used in each case. The rates determined at four temperatures - 25°, 40°, 60°, and 80°C. gave results which are shown in Table 8 and plotted in Figure 15. These will be discussed later on along with similar results for Orange II and Azo Geranine 2G.

Table 8.

Rate of Sorption of Orange I at 25°, 40°, 60° and 80°C.

Temp.	Amount sorbed expressed in millimoles per Kgm. dry film.								
	Time in minutes								
	15	30	60	120	240	480	960	1440	2880
25°C	--	8.84	17.0	37.4	68.0	105.4	154.7	186.5	204.0
40°C	--	48.9	68.0	85.0	119.0	139.4	155.1	163.2	163.2
60°C	68.0	85.0	98.6	105.4	105.4	105.4	--	--	--
80°C	29.0	32.0	34.0	34.0	--	--	--	--	--

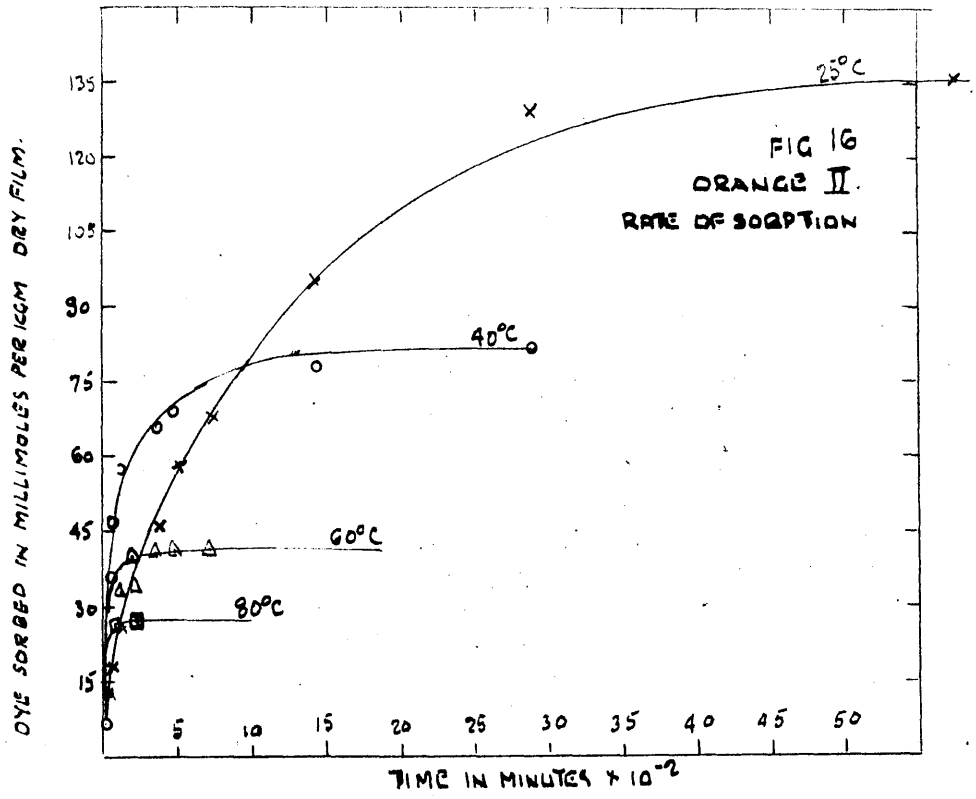


FIG 16
ORANGE II.
RATE OF SORPTION

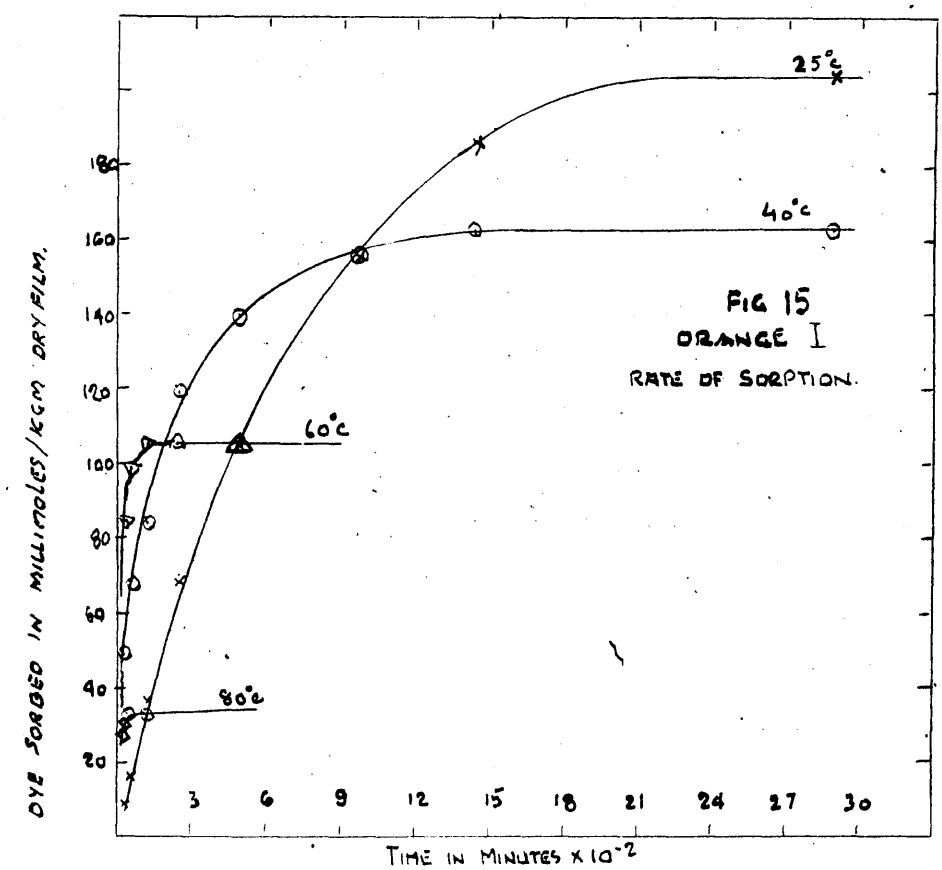
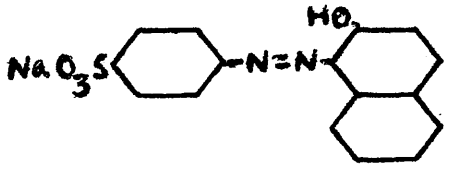


FIG 15
ORANGE I
RATE OF SORPTION.

(iii) The Rate of Sorption of Orange II. (Colour Index No.151)

The dye has the following constitution



Mol.wt.of dye 350

Mol.wt.of dye ion 327

As in the previous case, a dye solution of 1.0 gm. per litre concentration was prepared from pure dye, and diluted to 0.1 gm. per litre for rate experiments. The data obtained at the four temperatures of 25°, 40°, 60° and 80°C. are given in Table 9 and plotted in Figure 16.

Table 9.

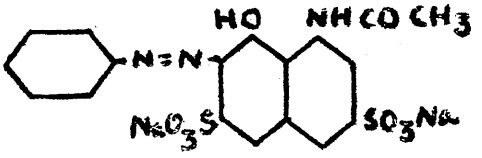
Rate of Sorption of Orange II at 25°, 40°, 60° and 80°C.

Time in mins.	Amount sorbed in millimoles per Kgm. of dry film.			
	25°C	40°C	60°C	80°C
15	--	6.8	13.6	17.0
30	13.6	17.0	21.4	23.8
60	17.0	35.6	28.8	27.2
120	27.2	48.0	34.0	27.2
240	40.8	54.4	40.1	--
360	46.6	66.2	40.8	--
480	58.5	69.0	40.8	--
720	68.0	72.2	40.8	--
1440	95.2	78.3	--	--
2880	129.2	81.6	--	--
5760	136.0	81.6	--	--

These results will also be discussed later.

(iv) The Rate of Sorption of Azo Geranine 2G. (Colour Index No.31)

The dye has the following constitution



Mol.wt.of dye 509

Mol.wt.of dye ion 463

A commercial sample of the dye was crystallised twice from glacial acetic acid and its purity estimated by titration with titanous chloride. The sample was found to contain 97.2% pure dye. As in the previous cases, a dye solution of 1.0 gm. per litre strength was prepared and some of it diluted ten times for experiments to determine rates. Table 10 contains the results of rates of sorption at 25°, 40°, 60° and 80°C.

Table 10.

Rate of Sorption of Azo Geranine 2G at 25°, 40°, 60° and 80°C.

	Amount sorbed in millimoles of pure dye per Kgm. of dry fil								
	Time in minutes.								
Temp.	30	60	120	240	480	960	1440	2880	5760
25°C	1.20	1.80	2.90	6.40	9.25	17.03	21.05	25.2	28.05
40°C	1.52	3.23	6.84	9.75	13.53	16.41	17.82	18.74	18.74
60°C	2.81	5.55	7.52	8.43	9.82	11.71	11.71	--	--
80°C	3.82	5.53	6.01	6.10	7.01	7.01	--	--	--

Figure 17 contains curves constructed from the above data.

The results will now be discussed together. The following points are worth noting :-

(a) It will be observed that the rates of sorption of all the three dyes exhibit a striking regularity with respect to the

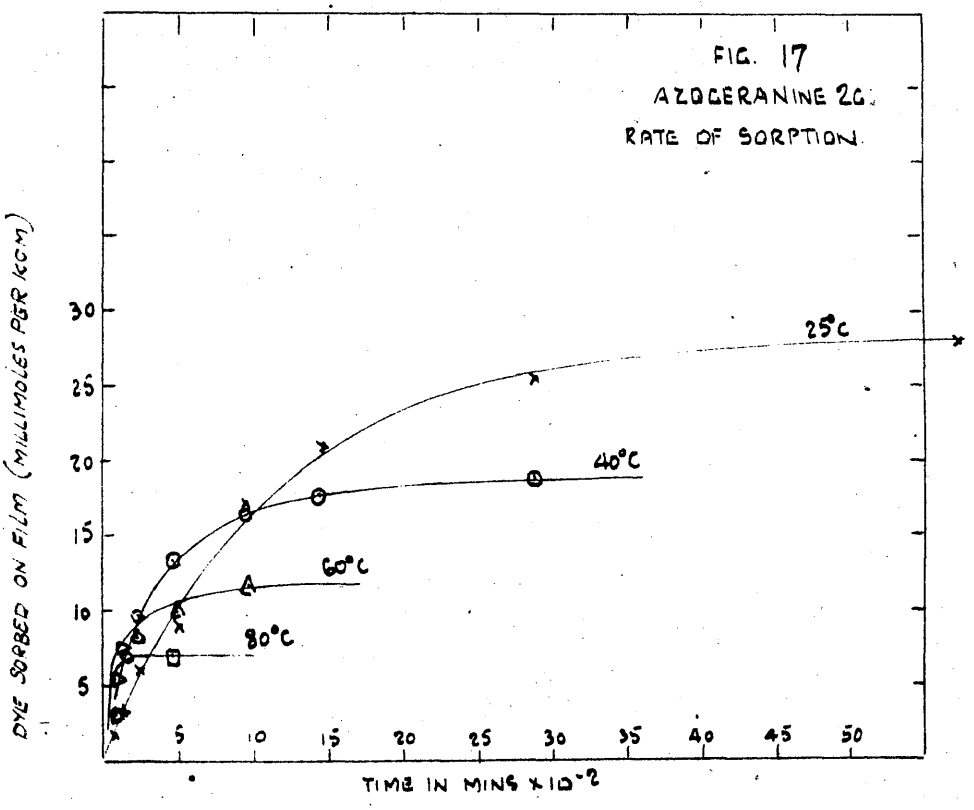
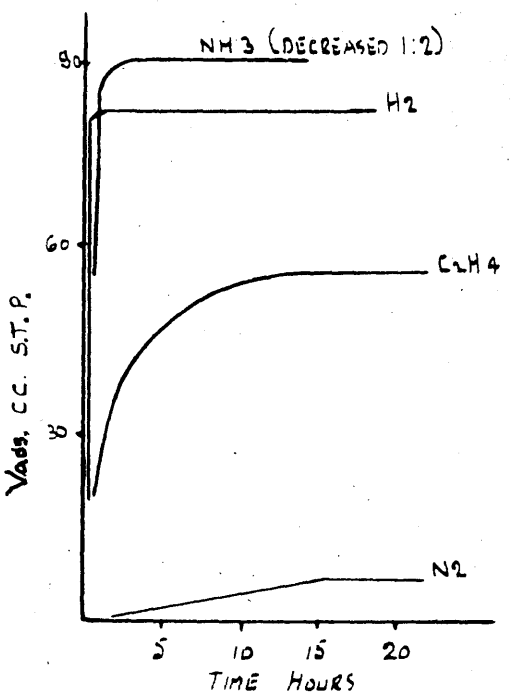


FIG. 17
AZOGERANINE 2G
RATE OF SORPTION
DYE SORBED ON FILM (MILLIMOLES PER KG.M)
TIME IN MINS X 10⁻²
25°C
40°C
60°C
80°C
5
10
15
20
25
30
35
40
45
50

effect of temperature. The rate increases with temperature in all the cases; a result invariably found in experiments on adsorption rates.

(b) As the sorption proceeds, the curves cross each other. This is because the amount sorbed at equilibrium decreases progressively with temperature.

(c) It is, however, interesting to note that the shape of the rate curves changes with temperature. The curves become steeper with rise of temperature because the velocity of reaction increases rapidly. This increase in velocity may be due to increased thermal agitation. The particle size of the dye may also influence the velocity. It is known that the dyes in solution consist of aggregated molecules, and that these aggregates break up to particles of smaller size as the temperature increases. The particles of smaller size will be sorbed at a greater rate than larger particles. A somewhat similar observation was made by Dohse and Mark (132), who found that if an adsorbent had long and very narrow pores, the size of the migrating molecules makes a great difference in the rate of adsorption. In Figure 18, taken from their paper, the rates of adsorption of some gases on Chabasite are shown. The rates are much higher, and consequently the curves much steeper, in the case of smaller molecules like ammonia and hydrogen, which resemble our curves at higher temperatures. The rate curves of somewhat larger slow-adsorbing molecules like nitrogen and ethylene are similar to the sorption curves of the dyes at lower temperatures. The pores of the anodic film can be classed as long and very



THE RATE OF ADSORPTION OF GASES ON CHABASITE

FIG. 18.

narrow as their length is approximately a hundred times their diameter.

(d) The rates of sorption and the equilibrium sorptions of Orange II are in general lower than those of Orange I, and those of Azo Geranine 2G are lower still. This may be due to the size and structure of the molecule. In the case of Orange I and Orange II, where the sizes of the two molecules are approximately equal, the o-hydroxy group in Orange II, by chelation with the azo group will tend to produce a more rigid molecule and thus impede the smooth passage of the molecules within the narrow pores of the film. Azo Geranine 2G has probably an added impediment in the form of a higher charge on the molecule. Sneddon (133) has observed that a dye with three sulphonic groups is sorbed in a far lesser amount than dyes with one or two sulphonic groups, probably because the greater attraction between the film and the dye particles at the outer surface does not allow the dye particles to move inside the film, thus blocking further sorption.

The applicability of Fick's diffusion equation can be tested by plotting sorption against square root of time. This has been done in Figures 19, 20 and 21 for all the three dyes. It is to be noted that as in the case of Tartrazine O the curve for each temperature and each dye is made up of two or three straight lines.* This supports the view expressed earlier that the film is built up of more than one layer.

Fick's diffusion equation can be made the starting point for developing an equation which can be used to calculate the

*(See footnote p.96)

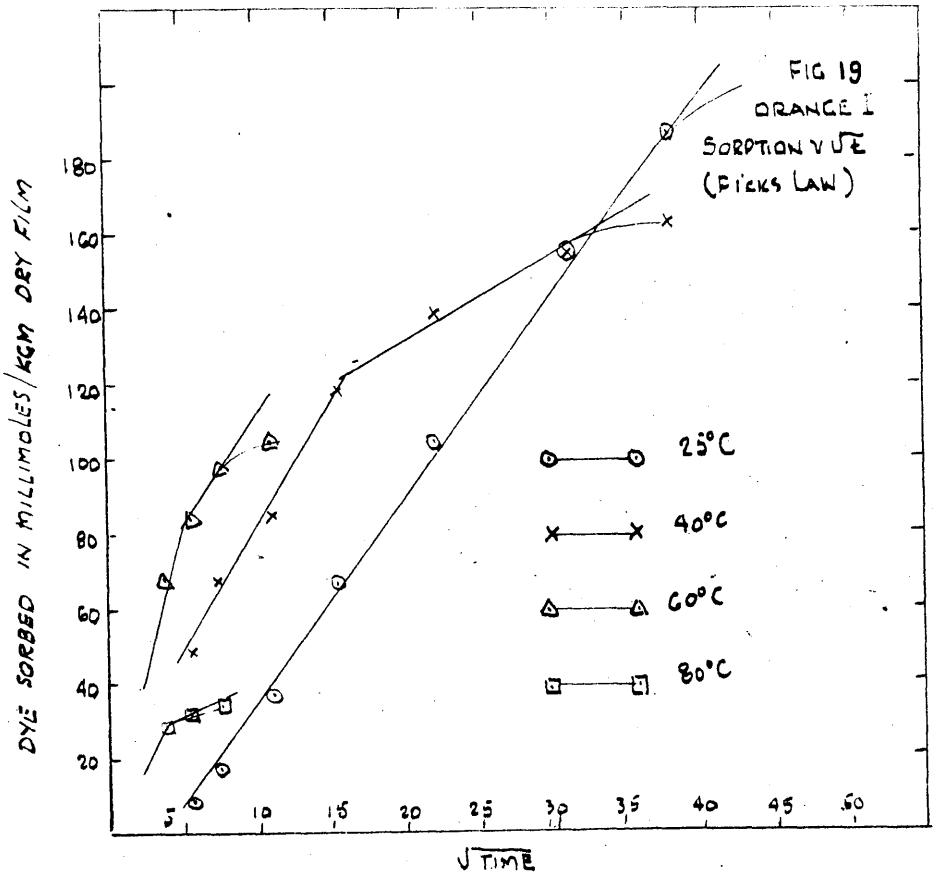


FIG 19
ORANGE I
SORPTION V √t
(FICKS LAW)
DYE SORBED IN MILLIMOLES/KGM DRY FILM
180
160
140
120
100
80
60
40
20
5
10
15
20
25
30
35
40
45
50
√TIME
25°C
40°C
60°C
80°C

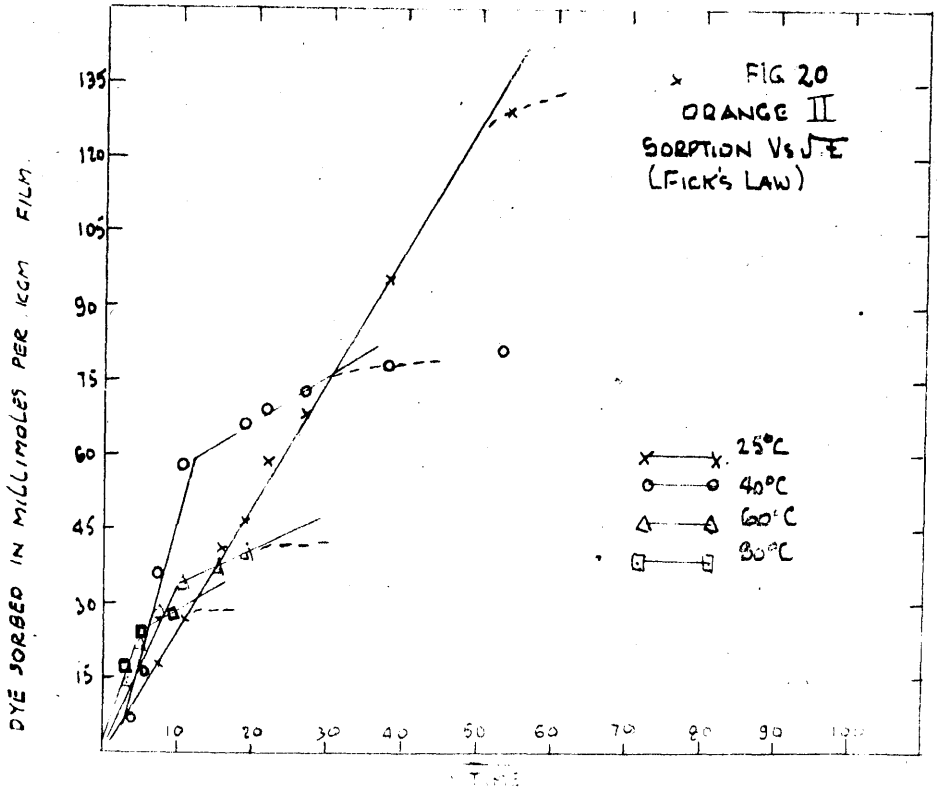


FIG 20
ORANGE II
SORPTION Vs √t
(FICK'S LAW)
DYE SORBED IN MILLIMOLES PER KGM FILM
135
120
105
90
75
60
45
30
15
10
20
30
40
50
60
70
80
90
100
TIME
25°C
40°C
60°C
80°C

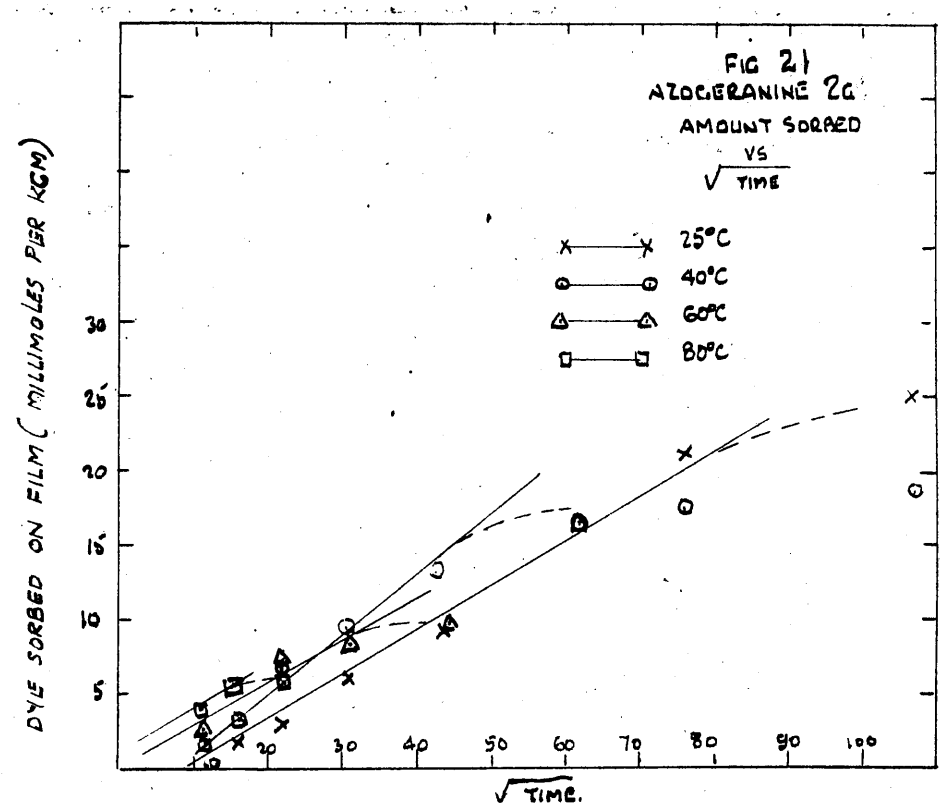


FIG 21
AZOGERANINE 2G
AMOUNT SORBED
VS
√ TIME
25°C
40°C
60°C
80°C
DYE SORBED ON FILM (MILLIMOLES PER KGM)
√ TIME.
5
10
15
20
25
30
30
40
50
60
70
80
90
100

diffusion constant. Accordingly A.V.Hill (64) has used the following equation for the calculation of diffusion of oxygen into a muscle tissue from a medium of constant composition:-

$$\frac{D_t}{D_\infty} = 1 - \frac{8}{\pi^2}\left[e^{-\frac{K\pi^2 t}{4b^2}} + \frac{1}{9}e^{-\frac{9K\pi^2 t}{4b^2}} + \frac{1}{25}e^{-\frac{25K\pi^2 t}{4b^2}} + \ldots\right]$$

where D_t and D_∞ are the amounts diffused, at time t and at equilibrium, respectively, through a plane sheet, b cm. thick exposed on one side, and K is the diffusion constant. As mentioned in the introduction this equation was derived by McBain (63) but was not tested by him.

As the equation involves an infinite series it might be difficult to handle; but fortunately, however, it is rapidly convergent when t is large. It is quite convenient for use for short times as well. Hill (loc.cit.) has calculated the values of D_t/D_∞, the fractional equilibrium sorption at time t, for different values of $\frac{Kt}{b^2}$. They are expressed in the following table:-

Table 11.

Values of $\frac{Kt}{b^2}$ against D_t/D_∞ at time t.

$\frac{Kt}{b^2}$	0.0045	0.009	0.0135	0.0225	0.045	0.09	0.135	0.225
$\frac{D_t}{D_\infty}$	0.075	0.105	0.130	0.169	0.239	0.332	0.414	0.534
$\frac{Kt}{b^2}$	0.315	0.450	0.675	0.900	1.125	1.350	1.800	2.250
$\frac{Dt}{D_\infty}$	0.628	0.732	0.846	0.911	0.949	0.971	0.990	0.997

The average fractional equilibrium sorption, $\frac{D_t}{D_\infty}$, is a function simply of $\frac{Kt}{b^2}$ and hence if the above values are plotted, a standard curve could be obtained from which the values of $\frac{Kt}{b^2}$ can be read for any values of $\frac{D_t}{D_\infty}$ or *vice versa*. This curve is available for any values of K and b . The standard curve from the data of Table 11 has been drawn as shown in Figure 22. From this curve, the values of $\frac{Kt}{b^2}$ can be obtained for the observed values of $\frac{D_t}{D_\infty}$ at time t and knowing t and b , the value of K , the diffusion constant, can be calculated. It is clear from Table 11 that as D_t approaches equilibrium, a small change in the value of $\frac{D_t}{D_\infty}$ corresponds to a relatively large change in the value of $\frac{Kt}{b^2}$, which leads to uncertain results. Hence the values of K , the diffusion constant may vary. An average representative value should, therefore, be selected.

It should be noted here that the equation outlined above is only applicable to diffusion after exposure to a constant concentration at the surface. Normally, our data will not be suitable for testing this equation, but we assume that owing to electrostatic attraction between the film and the dye particles by virtue of their opposite charges, an almost constant concentration of dye particles is maintained at the surface. If a part of this diffuses within the pores, fresh particles from the dye solution readily fill up the vacant positions. This was found to be the case in wool dyeing, by Speakman and Smith (142A).

With the help of Figure 22, values of $\frac{Kt}{b^2}$ were determined for various values of $\frac{D_t}{D_\infty}$ for all the three dyes at four

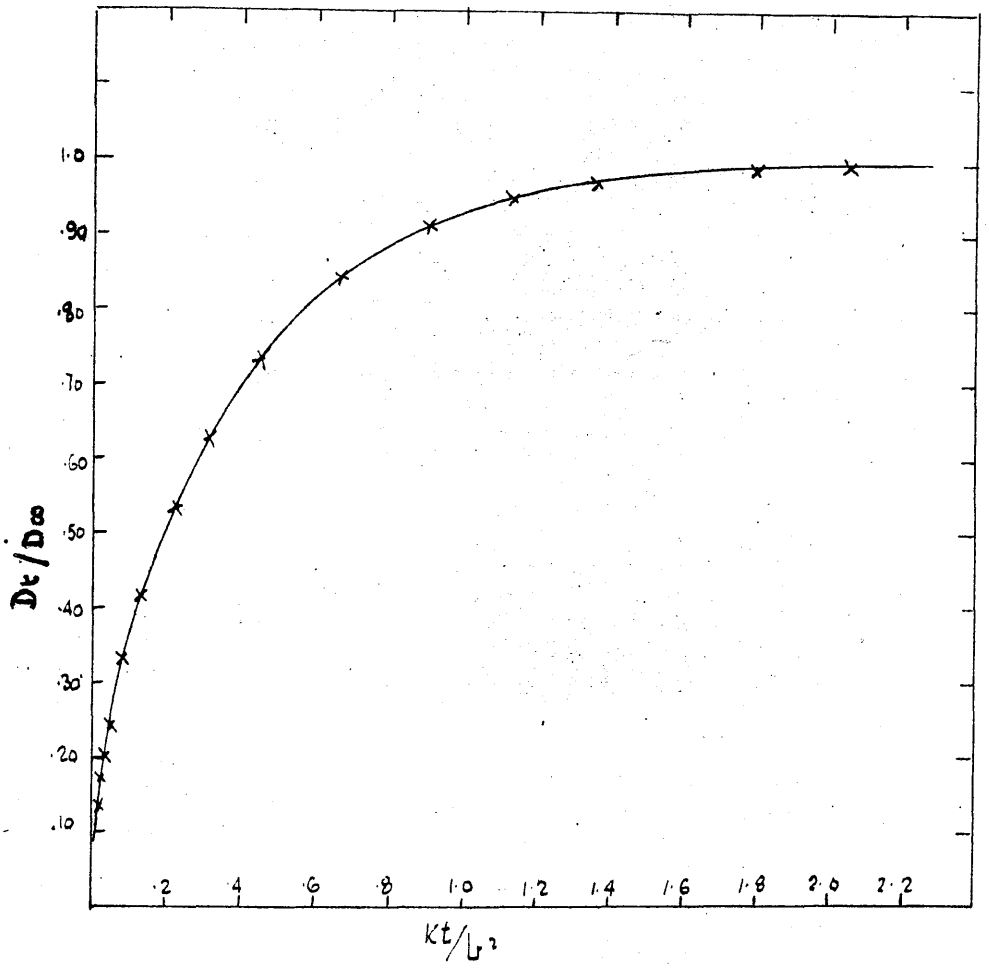


FIG. 22

CURVE SHOWING AVERAGE FRACTIONAL EQUILIBRIUM SORPTION AT VARIOUS TIMES. THE VALUES ARE BASED ON HILL'S PAPER (64)

temperatures, and the value of K calculated therefrom. The Table 12 contains the average values of K so obtained.

Table 12.

Diffusion Constants of Dyes at 25°, 40°, 60° and 80°C.

Name of the dye	Values of diffusion constant, K in cm^2 / min.			
	25°C	40°C	60°C	80°C
Orange I	0.9×10^{-14}	1.3×10^{-13}	0.8×10^{-12}	---
Orange II	2.0×10^{-14}	1.1×10^{-13}	5.2×10^{-13}	1.5×10^{-12}
Azo Geranine 2G	5.8×10^{-15}	5.1×10^{-14}	1.5×10^{-13}	5.4×10^{-12}

It is interesting to compare the values of the diffusion constant of the dye in the film with that of the dye in water. Valkó (54) has determined the value of the diffusion constant of Orange II in pure water at 25°C which is 4.4×10^{-4}. The diffusion constant K, can be calculated from the Stokes-Sutherland-Einstein equation

$$K = \frac{R\,T}{N} \times \frac{1}{6\,\pi\,r\,\mu}$$

where R is the gas constant, T, the absolute temperature, N, the Avogadro number, r, the radius of the particle, and μ, the viscosity of the medium.

It is clear from the equation that the value of diffusion constants of the above dyes in water will not very widely vary from the value for Orange II given above. If we compare this value with diffusion constants of dyes in the film in Table 12 for corresponding temperatures, it becomes evident that the very small value of the constant in the film must be due partly to the

very small size of the pores. As mentioned in the introduction, the two values put forward for the diameter of pores are of the order of 110 Å and 10 Å. It appears from this that the latter value is the more likely of the two. Acid dyes are almost molecularly dispersed in solution and, for example, Orange II with a radius of about 4.77 Å (Valko, loc.cit) should not have much difficulty in diffusing through the pores of the film if the diameter of the pores was of the order of 110 Å. It is true, of course, that the values of the diffusion constants in the film arrived at as above are only approximate because of the many simplifying assumptions made, and that simultaneous absorption of dye molecules by the film lowers the value of the apparent diffusion constant. However, the difference in the two values is sufficient to support the view expressed above that the diameter of the pores may be of order of 10Å

The influence of temperature on the diffusion constant and hence on the dyeing speed can be seen from the data given in Table 12. Increase in temperature results in an increase in both these factors, which is in conformity with observations made earlier. It is also of interest to note that, in general, the diffusion constant of Azo Geranine 2G in the film is lower than that of Orange II, which is, in turn, lower than that of Orange I. According to the Stokes-Sutherland-Einstein equation given above, this must be due to the larger radius of the particles of Azo Geranine 2G than the other two. This partly furnishes the reason for the slower speed of sorption of this dye on the film but; as we have said, this effect will not be very great and hence will only be partially responsible.

From the average value of the diffusion constant, K , in the film, the value of $\frac{Kt}{b^2}$ for different experimental times can be calculated. The corresponding values of $\frac{D_t}{D_\infty}$ can be determined from the standard curve in Figure 22, and the values of D_t for various values of t can be calculated. These values can be plotted, and, if the process is one of diffusion they should not differ very much from the observed values of D_t . This was done in the case of Orange I at 40°C, Orange II at 25°C and Azo Geranine 2G at 60°C. Tables 13, 14, 15 contain the observed and calculated values of D_t for Orange I, Orange II and Azo Geranine 2G respectively.

Table 13.

The observed and calculated diffusion of Orange I at 40°C.

$b = 8.5 \times 10^{-6}$cm. $K = 1.3 \times 10^{-13}$cm^2/min.

D_∞ = 163.2 millimoles/Kgm.film

	Amount sorbed expressed in millimoles per Kgm.film.					
t in mins	30	60	120	240	480	960
D_t observed	48.9	68.0	85.0	119.0	139.4	155.1
D_t calculated	42.4	60.4	85.5	118.0	146.9	160.0

Table 14.

The observed and calculated diffusion of Orange II at 25°C.

$b = 8.5 \times 10^{-6}$cm. $K = 2.0 \times 10^{-14}$

D = 136.0 millimoles /Kgm.film

t in mins.	Amount sorbed expressed in millimoles per Kgm.film.								
	30	60	120	240	360	480	720	1440	2880
D_t observed	13.6	17.0	27.2	40.8	46.6	58.5	68.0	95.2	129.2
D_t calculated	13.6	19.0	27.9	39.4	47.6	55.8	68.0	95.2	120.0

Table 15.

The observed and calculated diffusion of Azo Geranine 2G at 60°C

$b = 8.5 \times 10^{-6}$cm. $K = 1.5 \times 10^{-13}$

D = 11.71 millimoles/Kgm.film.

t in mins.	Amount sorbed expressed as millimoles per Kgm.film.				
	30	60	120	240	480
D_t observed	2.8	5.5	7.5	8.7	9.8
D_t calculated	3.2	4.7	6.6	9.0	10.8

These values have been plotted in Figures 23,24 and 25. The curves represent the calculated values of D_t while the corresponding observed values of D_t have been shown by means of points. The values for Orange II are the best fit, but even though the other dyes appear to diverge more, the divergence will not appear vary significant if it is borne in mind that the value

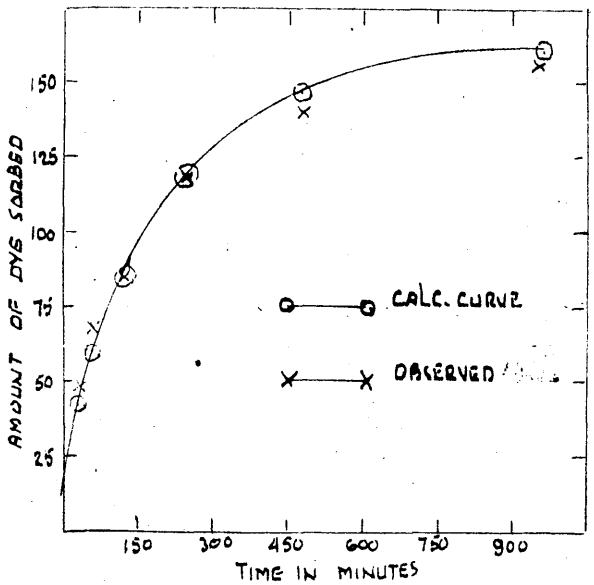


FIG. 23 CURVE SHOWING CALCULATED SORPTION OF ORANGE I AT 40°C WITH CORRESPONDING POINTS SHOWING OBSERVED VALUES

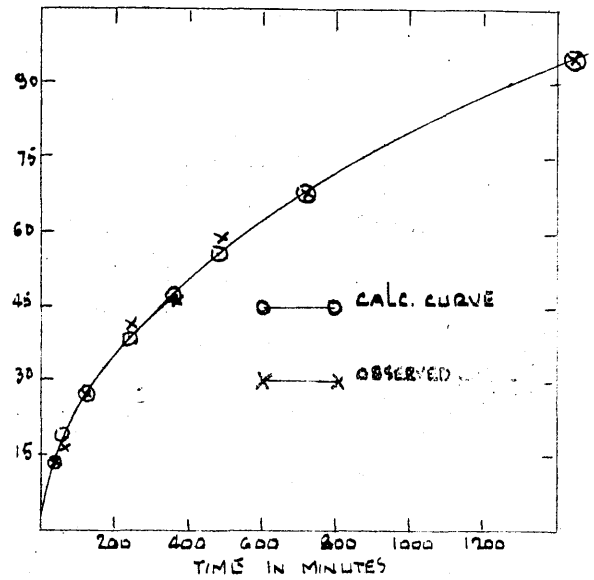


FIG. 24 CURVE SHOWING CALCULATED SORPTION OF ORANGE II AT 25°C WITH CORRESPONDING POINTS SHOWING OBSERVED VALUES

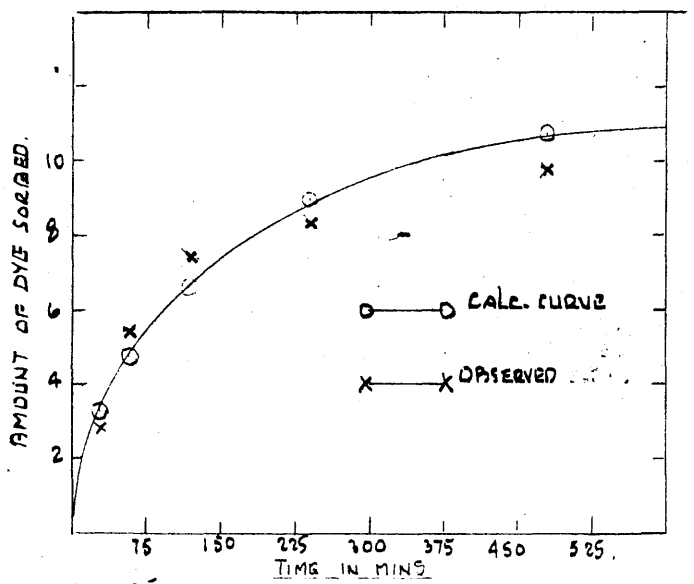


FIG. 25 CURVE SHOWING CALC. SORPTION OF AZOBERANING 20 AT 60°C WITH CORRESPONDING POINTS SHOWING OBSERVED VALUES.

of D_t are expressed in millimoles per Kgm. of the film which is in effect multiplication of the original values by approximately 25,000 and hence the divergence is magnified to that extent. Again, also due to the approximate nature of these calculations, this divergence should not be regarded as very significant. The curves in Figures 23, 24 and 25 show that the dyeing of the anodic film should be regarded as a diffusion process.

Even though it appears from the above that the dyeing of the film is by diffusion, it may be of interest to see whether adsorption plays any part at any time during the process. The theory of rate of adsorption on a free surface was first enunciated by Langmuir (134) and he derived an expression for the same by assuming that the experimentally observed rate of adsorption is the difference between the rate at which molecules condense on the surface and the rate at which they leave the surface. Therefore, if a small fraction of the surface $d\theta$ is covered by the sorbate in time dt the rate at constant pressure is given by

$$\frac{d\theta}{dt} = K_1 (1 - \theta) - K_2 \theta$$

where θ is the fraction of the surface covered with adsorbed dye and K_1 and K_2 are constants.

Integrating with the boundary condition that $\theta = 0$ when $t = 0$ we obtain,

$$\theta = \frac{K_1}{K_1+K_2} \left(1 - e^{-(K_1 + K_2)t} \right)$$

when $t = \infty$, $\theta = \theta_e$ = fraction of surface covered at equilibrium,

$$\theta_e = \frac{K_1}{K_1 + K_2}$$

Substituting this in the above equation, we obtain

$$\theta = \theta_e (1 - e^{-Kt})$$

where $K = K_1 + K_2$

Now if C_A represents the amount of dye taken up at equilibrium, C_F, the amount taken up at time t and C_M, the amount necessary to cover the entire surface by a unimolecular layer,

$$\theta = \frac{C_F}{C_M} \quad \text{and} \quad \theta_e = \frac{C_A}{C_M}$$

and we can write the above equation as

$$C_F = C_A (1 - e^{-Kt})$$

$$\text{or} \quad \ln \frac{C_A}{C_A - C_F} = Kt$$

This equation is in a form which could be applied to the data of rates of sorption of the three dyes on the film. This has been done in Figures 26, 27 and 28. The rate data at 25°, 40° and 60°C are plotted. The curves for 60°C do not contain sufficient number of experimental points to base any conclusion on them. The curves are interesting. All of them are straight lines for the initial period of sorption. Later on they deviate into another straight line. Langmuir's derivation is based on two concepts - the adsorbing surface behaves as a free and uniform surface with identical sorption centres at all sites of the surface, and that these sites are covered with a unimolecular

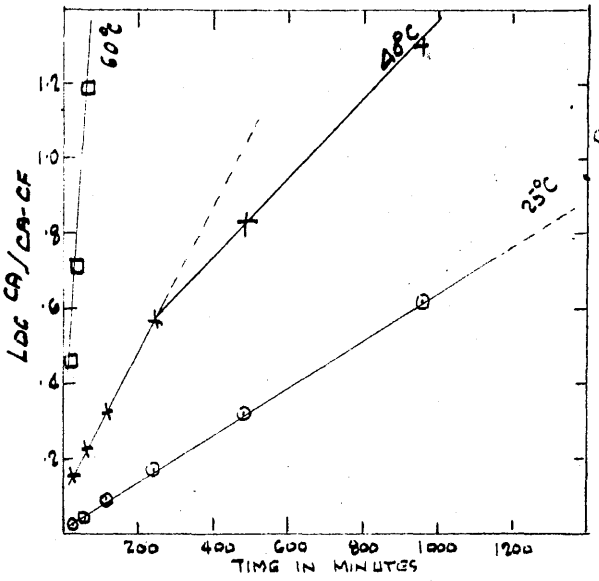


FIG. 26 THE RATE OF SORPTION OF ORANGE I PLOTTED ACCORDING TO LANGMUIR EQUATION.

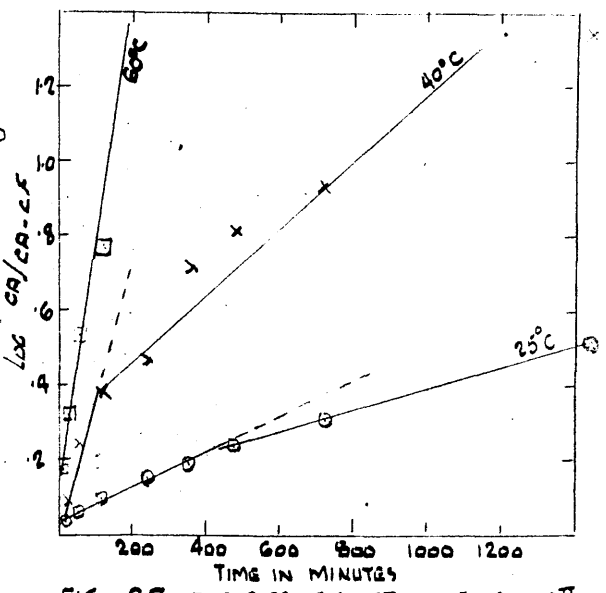


FIG. 27 THE RATE OF SORPTION OF ORANGE II PLOTTED ACCORDING TO LANGMUIR EQUATION

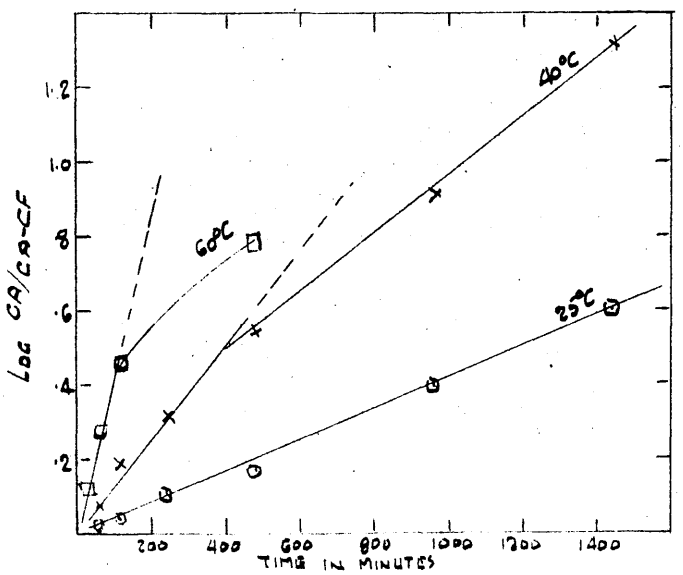


FIG. 28 THE RATE OF SORPTION OF AZOCERANINE 2G PLOTTED ACCORDING TO LANGMUIR EQUATION

layer of adsorbate. It appears quite reasonable to assume that the former concept of the uniformity of the surface appears to hold good for the surface of the film dealt with here; but nothing is known as regards the formation of a unimolecular layer during sorption. If for a moment we assume that a unimolecular layer is formed, the Langmuir equation will only be obeyed if the dye is adsorbed and only the surface forces and no others play a part. We have seen, however, that this is not the case. Diffusion is also involved in the mechanism. The break in Langmuir curves indicates this. It appears, therefore, that in the initial period of sorption, the dye molecules are adsorbed on the free and uniform surface of the film, but as other mechanisms begin to operate later, conformity to the Langmuir mechanism is interfered with. The Langmuir equation in its simple form is thus limited in its applicability and could not give any further indication of the nature of the mechanism involved.

The rate data could, however, be utilised to calculate the activation energy of the processes. We will briefly discuss here the significance of the activation energy as it is widely applied to chemical reactions. Hinshelwood (135) has done this in a very simple and clear manner thus "The configuration of a stable molecule represents a minimum of potential energy. If stable molecules rearrange themselves by a chemical transformation to give fresh ones, the new configurations also represent minima of potential energy. There must be intermediate states where the potential energy is greater than in the initial or

final states. Somewhere in the intermediate region there must be a maximum which may be likened to a pass over which the molecules must travel in the course of the reaction. The top of this pass is what is sometimes called the transition state..... The energy which must be supplied to the reacting substances to make them capable of chemical transformation into the products is called the activation energy". In all the chemical reactions, this energy is influenced by thermal agitation and this is demonstrated clearly by the study of the influence of temperature on the rate of reaction. Arrhenius (136) suggested that an equilibrium exists between the normal molecules and what he called "active" molecules, and that only the latter undergo chemical change. The rapid increase in the rate of chemical change with rising temperature is, therefore, caused by the shift in equilibrium between the two kinds of molecules. He empirically formulated the equation

$$\frac{d \log K}{d T} = \frac{A}{RT^2}$$

where K is the velocity constant and A, the energy of activation which represents the shift in equilibrium mentioned above. The equation can be integrated as

$$\ln K = C - {}^{A}/_{RT}$$

This form of the equation can be tested by plotting logarithms of the velocity constant against the reciprocal of the absolute temperature. If the equation is obeyed a straight line should be obtained and the slope of the line would be $\frac{A}{2.303\ RT}$ from which the activation energy, A , could be calculated in calories per gm. mole. Now if t is the time required for a

definite fraction of the product of the reaction at equilibrium to be produced, then

$$t \propto \frac{1}{K}$$

and $\log K = B - \log t$ where B is a constant.

This means that the slope of the curve will be unchanged if $\log t$ is plotted instead of $\log K$, but the curve will run up instead of down with increasing values of $\frac{1}{T}$.

The data from tables 8, 9 and 10 are utilised to test the applicability of the Arrhenius equation and to calculate the energy of activation of each process. The time, t (in mins), required to accomplish the reaction up to half the equilibrium value was read in each case from the rate curves. (The curves at higher temperatures, particularly, were drawn to a very magnified scale to determine these values with accuracy). These values have been expressed in Table 16.

Table 16.

Values of $\log t$ and $\frac{1}{T}$ for Orange I, Orange II and Azo Geranine 2G for the calculation of energy of activation.

Temp. °C	$\frac{1}{T} \times 10^3$ (Abs.temp)	Orange I		Orange II		Azo Geranine 2G	
		t in mins.	log t	t in mins	log t	t in mins	log t
25°C	3.356	465	2.6675	720	2.8573	768	2.8854
40°C	3.195	100	2.0000	75	1.8751	228	2.3579
60°C	3.003	8	0.9031	22	1.3424	60	1.7782
80°C	2.833	2	0.3010	5	0.6990	12	1.0792

These values are plotted in Figure 29 and the slope

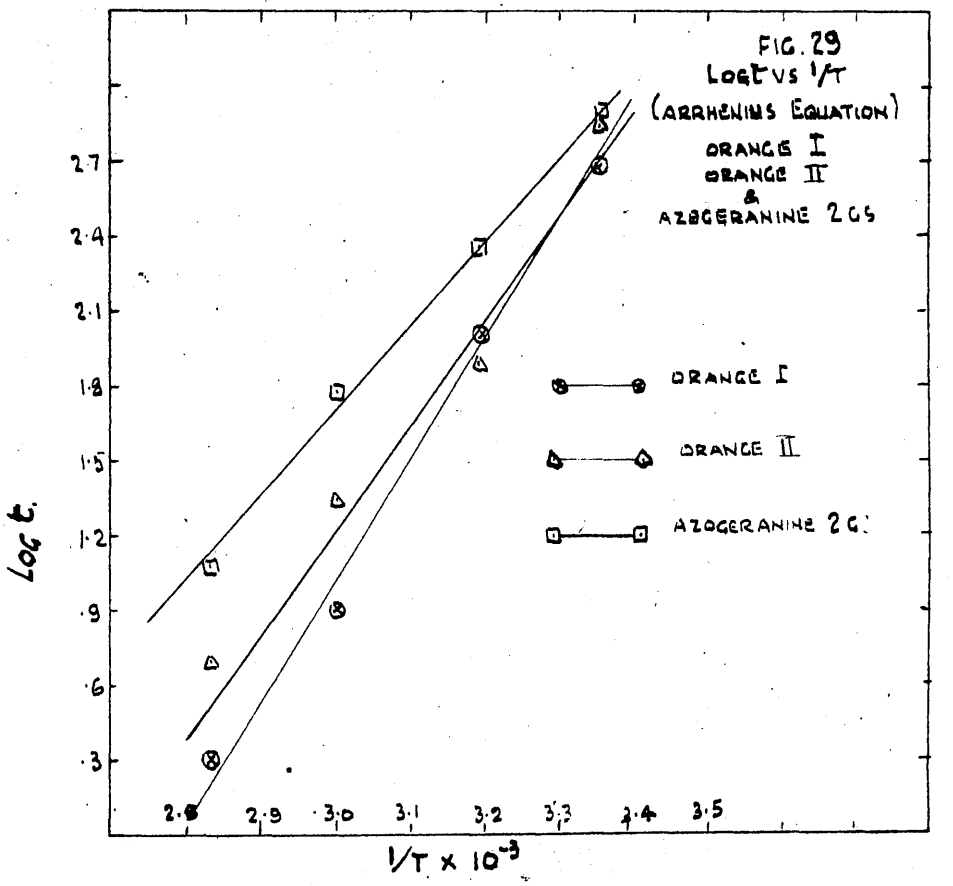


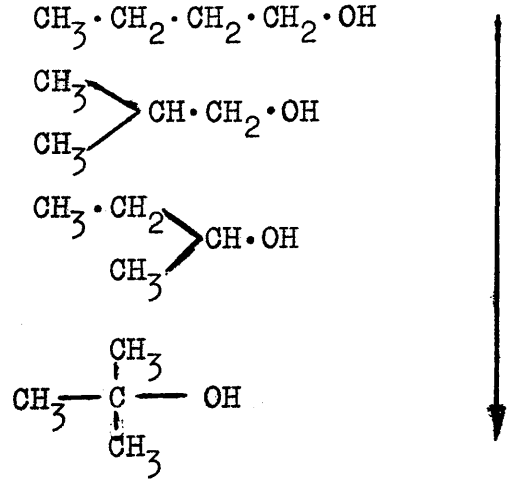
FIG. 29
Log t vs 1/T
(ARRHENIUS EQUATION)
ORANGE I
ORANGE II
&
AZOGERANINE 2G
ORANGE I
ORANGE II
AZOGERANINE 2G
Log t.
2·7
2·4
2·1
1·8
1·5
1·2
·9
·6
·3
2·8
2·9
3·0
3·1
3·2
3·3
3·4
3·5
1/T x 10⁻³

determined for each dye. The values of energy of activation calculated therefrom are given below.

Orange I	21,100	cals. per gm.mole
Orange II	21,700	cals. per gm. mole
Azo Geranine 2G	18,300	cals. per gm. mole

The similar magnitude of activation energies in the case of Orange I and Orange II is significant. This shows that the nature of bond between these dyes and the film is of the same type. The slightly higher value of Orange II may or may not be significant. It may be that the internal hydrogen bond in the Orange II molecule might be making the situation slightly difficult. However, we will not attach any importance to such a small difference. On the other hand, it is difficult to explain the somewhat lower value for Azo Geranine 2G. This may be due to two reasons:-

(a) It has been observed by Hunter (82) that in the butyl alcohols, owing to the electron-repulsive character of the methyl group, the acidity in the hydroxylic hydrogen atom decreases in the following order



This is also the order of decreasing association which is due to the hydrogen bonding within molecules. The Azo Geranine 2G molecule contains a methyl group. Perhaps due to the effect of this group, the N.....H - O bond between the o-hydroxy group and the azo nitrogen may be weaker than a similar bond in Orange II and hence this may be less firmly formed. The energy of activation may thus be smaller. However, we are conscious that this reason does not appear very convincing.

(b) The Azo Geranine 2G molecule has two sulphonic groups in its structure. This will mean that the molecule will have greater acidity than either Orange I or Orange II. This will favour the formation of a bond between the dye and the film and consequently lesser activation energy may be required for its formation. This may be the reason for lower value obtained above.

It will be noted that all the points in Figure 29 do not lie exactly on straight lines. It will be realised that factors such as the orientation of molecules at the moment of impact and the state of their internal vibrations would be expected to play an important role. Again all the reactions cannot be expected to be strictly built upon the same kinetic plan. The reactions have their kinetic peculiarities, which vary differently with changing conditions. However, the possibility of calculation of energies in the way outlined above provides a useful instrument to compare the nature of the reactions involved.

It will be worth while to summarise here the information about the mechanism of sorption of dyes on the film obtained

from a consideration of the kinetics of the process. We note that:-

(1) The rates of sorption of all the dyes increase with increasing temperature but equilibrium amounts decrease in that order. Both the rates and equilibrium sorptions decrease in the order Azo Geranine 2G < Orange II < Orange I. This may be due to molecular size, position of groups or the charge on the molecules. The net effect may be due to one or more of these causes.

(2) The steeper rate of sorption at higher temperatures may be due to breaking up of particles to smaller size.

(3) Application of Fick's diffusion theory indicates that the film may be built up of layers.

(4) The calculation of diffusion constants in the manner of Hill (64) and Neale and Stringfellow (62) and comparison of calculated values of dye sorbed at time t to corresponding observed values showed that dyeing is essentially a diffusion process. The comparison of the diffusion constants of the dye in the film and in water indicates that the pores must have a very small size and the value of 10 Å appears to be more likely of the two suggested in the literature.

(5) The process may be simple adsorption in the initial stages, as shown by the application of Langmuir's equation. It becomes complex later on.

(6) Calculation of activation energies by applying the Arrhenius equation shows that the nature of the bond between Orange I and

Orange II and the film is essentially the same. The lower value in the case of Azo Geranine 2G may be due to the greater acidity of the molecule.

2. Sorption Equilibrium.

(i) Orange I.

Dyebaths containing different initial concentrations of the dye were prepared by diluting to necessary strength the original solution (1.0 gm.per litre) prepared during the rate work described earlier. Sorptions of dye at equilibrium on anodic film from these solutions were determined at four temperatures, 25°, 40°, 60° and 80°C. Table 17 below contains the results obtained.

Table 17.

Equilibrium sorptions of ORANGE I at 25°, 40°, 60° and 80°C.

a = concn. of dye on film, C_F , in millimoles per Kgm.dry film

b = concn. of dye in solution, C_B, in millimoles per litre.

25°C	a 108.8	204.0	442.0	714.0	986.0			
	b 0.0513	0.1040	0.2000	0.2570	0.3135			
40°C	a 163.2	299.2	646.0	476.0	816.0	1020		
	b 0.1486	0.3193	0.5985	0.4560	0.7410	0.855		
60°C	a 105.4	183.7	289.2	476.2	544.0	612.2	680.0	818.0
	b 0.1971	0.4172	0.8999	1.315	1.543	1.771	2.000	2.171
80°C	a 34.0	54.4	102.0	136.0	208.0			
	b 0.2570	0.5244	1.057	1.600	2.114			

Sorption isotherms were constructed from the data from this Table and are shown in Figure 30. These will be analysed with similar results from other dyes later on.

(ii) Orange II

Solutions of varying concentration were prepared from the original solution (1.0 gm. per litre) as in the previous case and

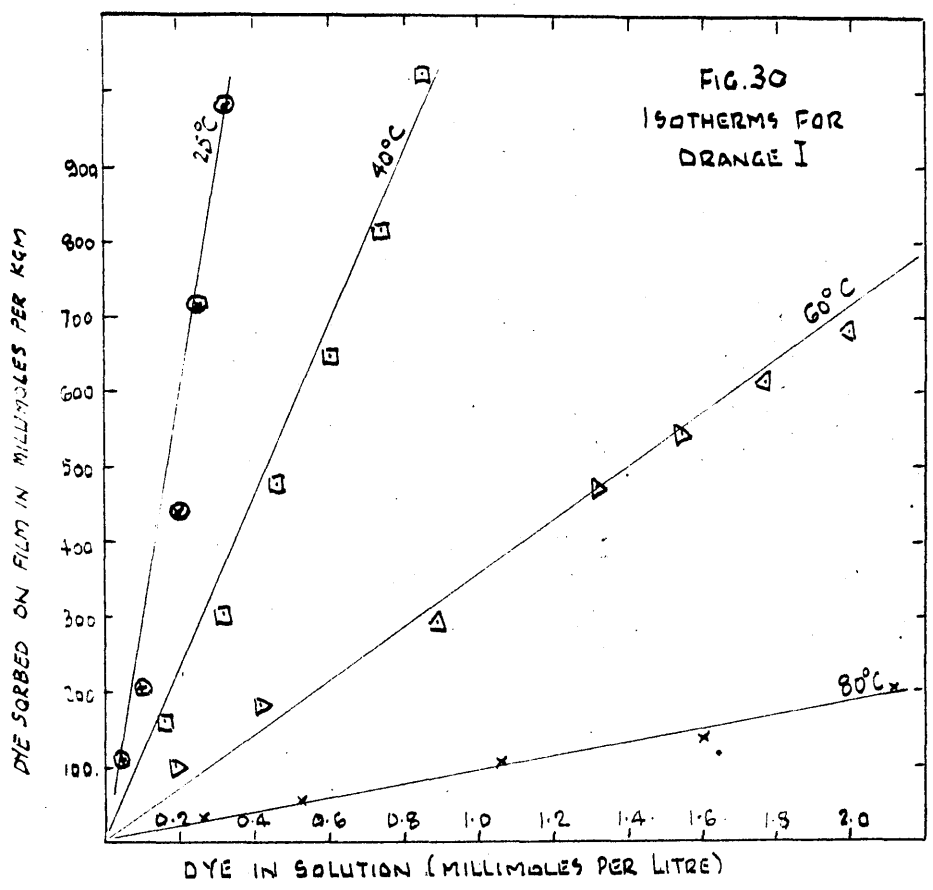


FIG. 30
ISOTHERMS FOR
ORANGE I
25°C
40°C
60°C
80°C
DYE SORBED ON FILM IN MILLIMOLES PER KGM
DYE IN SOLUTION (MILLIMOLES PER LITRE)
100
200
300
400
500
600
700
800
900
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0

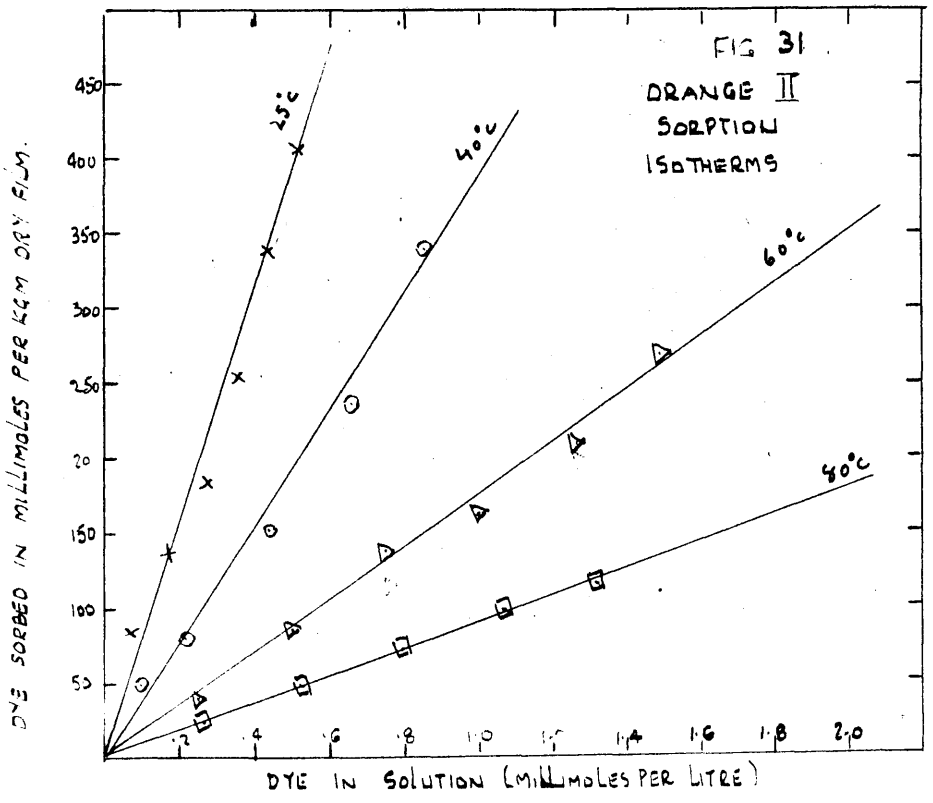


FIG 31
ORANGE II
SORPTION
ISOTHERMS
25°C
40°C
60°C
80°C
DYE SORBED IN MILLIMOLES PER KGM DRY FILM.
DYE IN SOLUTION (MILLIMOLES PER LITRE)
50
100
150
200
250
300
350
400
450
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0

sorptions at equilibrium determined in the same way. The results of experiments at temperatures of 25°, 40°, 60° and 80°C are contained in Table 18.

Table 18.

Equilibrium sorptions of ORANGE II at 25°, 40°, 60° and 80°C.

a = concn. of dye on film, C_F, in millimoles per Kgm.dry film.
b = concn. of dye in solution, C_B, in millimoles per litre.

25°C	a	85.0	136.0	185.4	255.0	340.0	408.0
	b	0.0713	0.1714	0.2715	0.357	0.428	0.515
40°C	a	51.0	81.6	153.0	238.0	340.0	
	b	0.100	0.217	0.4425	0.657	0.858	
60°C	a	40.8	88.4	136.0	163.2	210.8	252.0
	b	0.2515	0.497	0.740	1.00	1.258	1.500
80°C	a	27.2	51.0	75.0	102.0	112.4	
	b	0.2570	0.518	0.794	1.055	1.326	

Isotherms drawn from the data of this Table are contained in Figure 31. These will also be discussed later.

(iii) Azo Geranine 2G.

Equilibrium sorptions on the film at the same four temperatures from the dyebaths with various starting concentrations were determined as in the previous two cases. The observations are recorded in Table 19 and isotherms drawn in Figure 32.

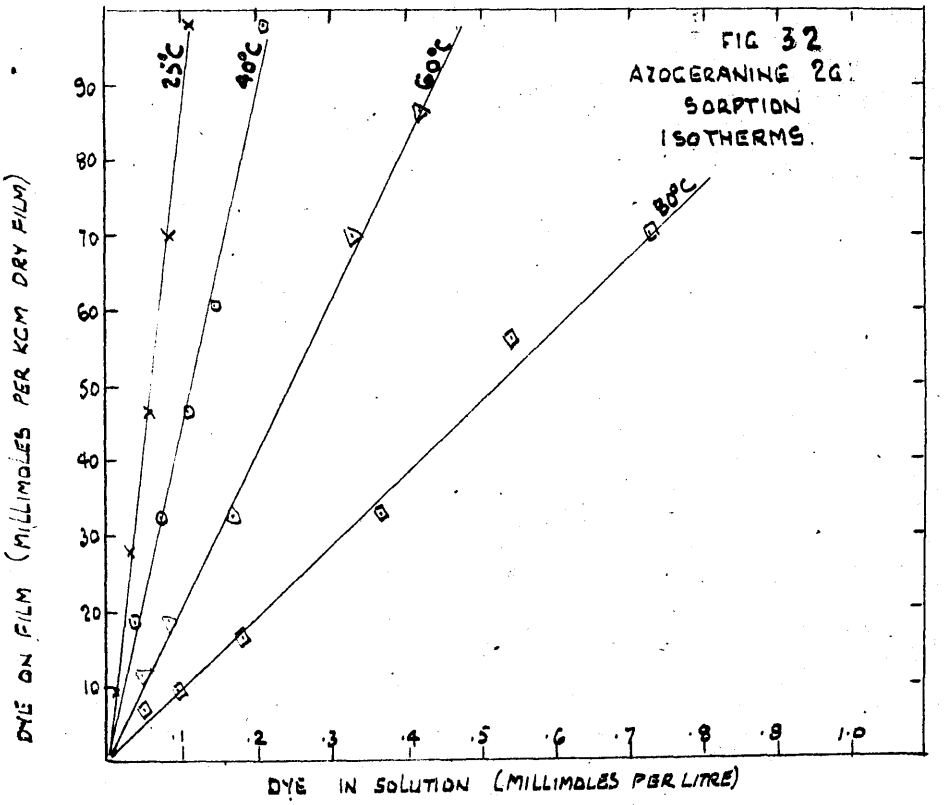


FIG 32
AZOGERANINE 2G.
SORPTION
ISOTHERMS.
25°C
40°C
60°C
80°C
DYE ON FILM (MILLIMOLES PER KGM DRY FILM)
DYE IN SOLUTION (MILLIMOLES PER LITRE)
10
20
30
40
50
60
70
80
90
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0

Table 19.

Equilibrium sorptions of AZO GERANINE 2G at 25°,40°,60° and 80°C.

a = concn. of dye on film, C_F, in millimoles per Kgm.dry film

b = concn. of dye in solution, C_B, in millimoles per litre.

25°C	a 9.36	28.5	46.8	70.2	98.3	
	b 0.0128	0.0334	0.0588	0.088	0.114	
40°C	a 18.7	32.7	46.8	60.9	98.3	126.3
	b 0.0412	0.0707	0.108	0.145	0.212	0.286
60°C	a 11.7	18.7	32.7	70.2	107.5	86.5
	b 0.0471	0.0823	0.1685	0.324	0.498	0.418
80°C	a 7.01	9.36	16.4	32.75	56.2	70.2
	b 0.051	0.092	0.1825	0.365	0.542	0.728

Now let us examine isotherms of all the dyes. The following points are to be noted:-

(a) All the isotherms are straight lines. The higher the temperature, the lower is the position of the isotherm. This is a typical characteristic of the adsorption isotherms. Brunauer (137) has broadly classified the isotherms usually met in the literature, and Figure 33 shows some of the types mentioned by him. If the sorbate is in solution in the sorbent, the isotherm takes the form of a straight line as in (a) in the Figure. The system obeys Henry's Law and the line has a constant slope. Curve (b) shows the isotherm of a chemical reaction between sorbent and sorbate. The rest of the three curves, (c) , (d) and (e) give simple types of van der Waals adsorption isotherms. If the isotherm obeys the Freundlich

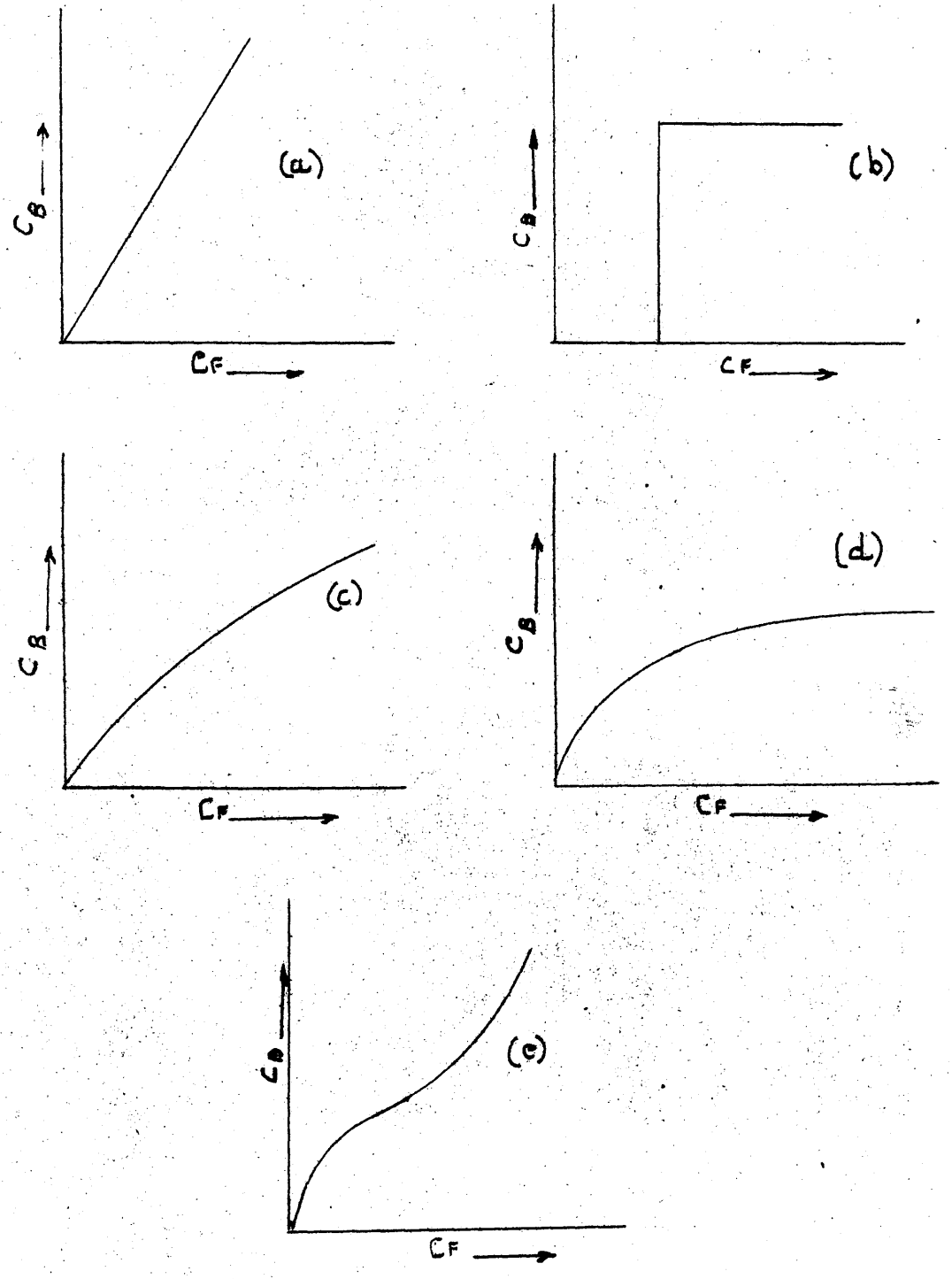


FIG 33 SOME TYPES OF SORPTION ISOTHERMS.

equation,

$$C_F = KC_B^{1/n}$$

where C_F and C_B are the amounts of sorbate on the film and in solution respectively at equilibrium, and K is a constant, the curve takes the form shown in (c). The amount of sorbate adsorbed becomes proportional to a power of concentration in the solution ($n > 1$). The curve (d) represents the adsorption of the Langmuir type where at higher concentrations in the bath, the sorbent approaches saturation and the line tends to be parallel to the bath concentration axis. These two curves represent unimolecular adsorption. The curve (e), an isotherm of the sigmoid shape, has been generally attributed to multimolecular adsorption. Brunauer and his collaborators (138) have proposed a theory of this type of adsorption, which embraces all types of isotherms generally found in the literature. Unimolecular adsorption is a special case of this treatment by Brunauer. Sorption isotherms in Figures 30, 31 and 32 show that the dye dissolves in the film. A closer inspection of the position of the points will show that in some of the isotherms, the points lie on a slightly sigmoid-shaped curve. Does this mean that the sorption is multimolecular in those cases? Detailed analysis of the isotherms might provide us with the information. We shall attempt this later.

(b) Here again, as in the case of rates, we find that the three dyes are sorbed in the order Azo Geranine 2G < Orange II < Orange I at equilibrium. As pointed out there, this might be

due to molecular size or charge on the molecule or both. The determinations of the energy changes involved might provide a clue to this behaviour.

Application of the Langmuir equation to the equilibrium sorption data is interesting. Skinner and Vickerstaff (84) have derived an expression which is a special case of Langmuir's equation and is applicable to data on sorption from solutions. The equation is

$$C_M \cdot \frac{C_B}{C_F} = \frac{K_2}{K_1} + C_B$$

where C_F and C_B are concentrations of dye on the film and in solution respectively, C_M is the concentrations of dye when a unimolecular layer is formed and K_1 , K_2 are constants.

The equation can be rearranged as

$$\frac{1}{C_F} = \frac{K_2}{K_1} \times \frac{1}{C_M} \times \frac{1}{C_B} + \frac{1}{C_M}$$

or $$\frac{1}{C_F} = \frac{1}{C_M \times K} \cdot \frac{1}{C_B} + \frac{1}{C_M} \quad \text{where} \quad \frac{K_1}{K_2} = K$$

It is clear from the above equation that if reciprocals of C_F and C_B are plotted as co-ordinates, a straight line should result. The slope of the line would give the value of $\frac{1}{C_M \times K}$ and the intercept, $\frac{1}{C_M}$. The data from Tables 17, 18 and 19 are accordingly plotted in Figures 34, 35 and 36 , and the results in all cases are very good straight lines particularl at the higher concentrations. Skinner and Vickerstaff note that the existence of a straight-line relationship at high

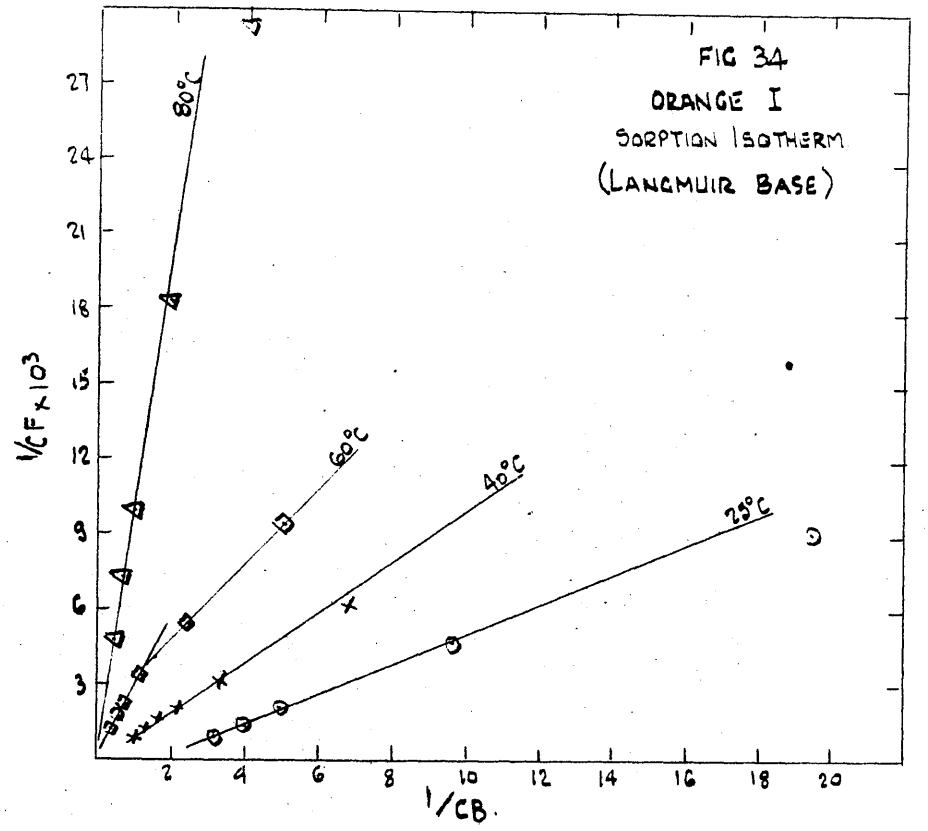


FIG 34
ORANGE I
SORPTION ISOTHERM
(LANGMUIR BASE)

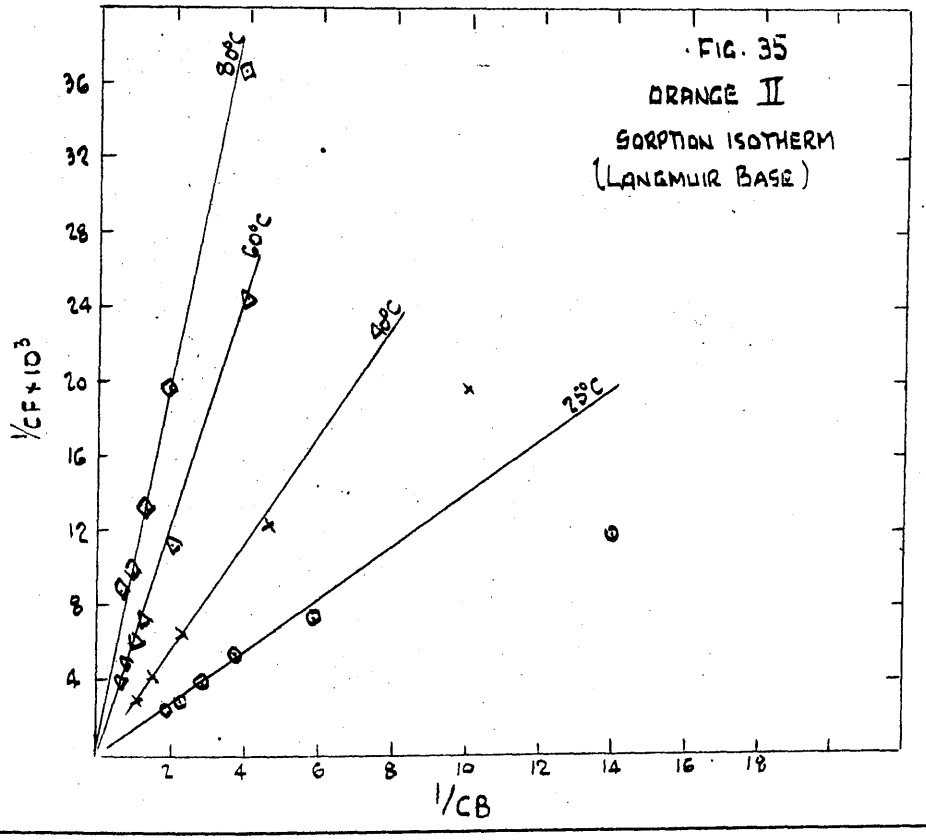


FIG. 35
ORANGE II
SORPTION ISOTHERM
(LANGMUIR BASE)

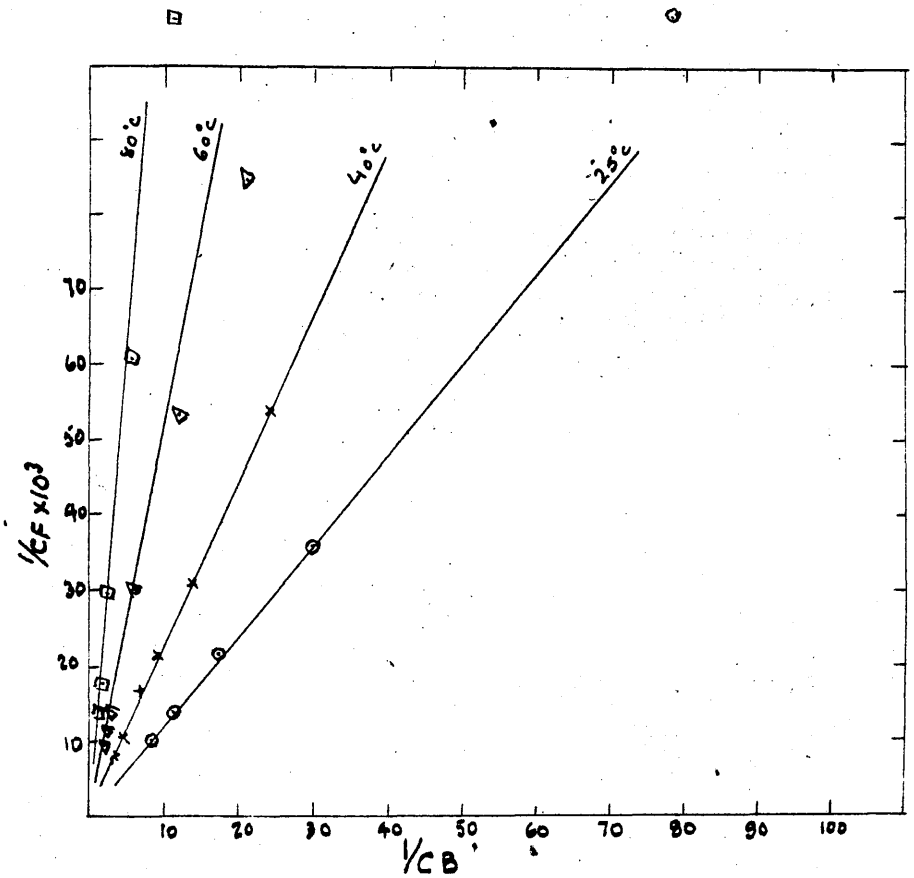


FIG 36

AZOGERANINE 2G
SORPTION ISOTHERM
(LANGMUIR BASE)

dyebath concentrations is not very significant. It should, however, be noted that in the present case many straight lines extend to low concentration regions as well. It must be emphasised here that obtaining a satisfactory straight line is a necessary but not a sufficient proof that the Langmuir equation is applicable to the data in question. To ascertain whether the applicability of the equation is genuine or not, the values of constants C_M and K should be determined. If the values so obtained are wholly unreasonable, we must come to the conclusion that the theory is not applicable.

Both the constants C_M and K are functions of temperature, C_M changing slightly, K very much, with temperature. Their combined effect is perhaps seen in increasing slopes of the lines from 25^oC to 80^oC. It is the intercept which decides beyond all doubt that the Langmuir fit is fictitious. Almost all the lines pass through the origin. This means that $\frac{1}{C_M}$ is zero i.e. C_M is ∞ . Since C_M represents the surface available for sorption, this means that the film has an infinite surface area. It is obvious that this cannot be true and it is concluded therefore that the Langmuir theory is not applicable. One might wonder why then in all the cases without exception very good straight lines are obtained. This may be accidental; or it may be that the primary conditions for the applicability of Langmuir's theory - uniform homogeneous surface, and identical nature of sites resulting in a uniform heat of reaction - exist in the present case. (Uniformity of heats of reaction will be demonstrated later). However, the take-up of

the dye by the film does not appear to be a case of van der Waals adsorption and hence we should not expect the theory to apply. That was probably why absurd values of the constant C_M are obtained. This is in conformity with what we found from the rate data.

Since the above treatment shows that van der Waals forces are not responsible for the attachment of the dye to the film, we must look somewhere else for it. Another line of attack in the study of sorption equilibrium is to determine the energy changes involved. This can be done by the thermodynamic treatment of the data.

The sorption of dye by anodised aluminium will be governed by the affinity of the dye for the film. The word "affinity" has been used in the past in a very vague manner to denote the chemical attraction between substances. This does not provide a satisfactory definition of the concept, but by considering certain reactions it was possible to arrange substances in order of decreasing or increasing affinity. For example, in the dyeing of textile fibres, the affinity was empirically measured by the exhaustion of dyebaths under arbitrary conditions or in terms of rate of sorption of dyes. It should be possible to define "affinity" in precise terms if the sorption of dye by the film be considered from a physico-chemical aspect. Like all other reactions, the film would sorb a dye if at the start of the reaction, a chemical potential difference existed between the dye in solution and the dye in the film. To be more precise and practical the chemical potential difference is

measured when the dye is in a standard state, in which activity is arbitrarily taken as unity. It can be shown that (eg.139) when a substance is at unit activity, the chemical potential is equal to the thermodynamic potential or, what is the same thing, the free energy. The free energy of a substance in solution as related to its standard state is given by the following equation

$$F = F^{o} + R\,T\,\ln a = \mu$$

where F = free energy of the substance in solution

F^{o} = standard free energy of the substance

a = activity of the substance in solution relative to its standard state of unit activity.

On this basis the chemical potential of the dye in solution may be expressed as

$$\mu_B = \mu_B^{o} + R\,T\,\ln a_B$$

and that of dye in the film as

$$\mu_F = \mu_F^{o} + R\,T\,\ln a_F$$

When the film and the solution are in equilibrium

$$\mu_F = \mu_B$$

so that

$$-(\mu_F^{o} - \mu_B^{o}) = -\Delta\mu^{o} = R\,T\,\ln a_F - R\,T\,\ln a_B$$

This equation provides a means of calculating affinity if we could suitably fepresent the activities in the two phases.

In solution, the acid dyes, which are sodium salts, are ionised and because the solutions are dilute, we can regard them as ideal. The activity coefficient, therefore, may be taken as

unity and the activity of the dye in solution is equal to its ionic concentrations

$$a_B = \left[Na_B^z\right] \cdot \left[C_B\right]$$

where $\left[Na_B\right]$ and $\left[C_B\right]$ are ionic concentration of the ionised dye in solution and z is the basicity of the dye anion.

It is difficult to represent activity in the film phase. Gilbert and Rideal (85) have shown that in cases like wool, where a specific number of sites exists it is justified to represent activity as $\theta/1-\theta$ where θ is the fraction of total sites occupied by dye ions. But the case of wool bears no comparison with anodic films. The sites in the case of the film are not ionic and even though one might be tempted to regard the anodic film as possessing of a specific number of non-ionic sites in view of its definite and rigid structure, it is not so. It has been seen that even when a chemical combination of the dye with the film is taking place between a mordant dye and the film, the values of sorption obtained bear no relation to the amount of the film. The film does not possess sites for the sorption of cations, which will also diffuse within the film along with the dye anions and hence will lie loosely in the pore space. The activity of the cations, therefore, could not be represented by any function of this nature. Therefore the only way to solve this difficulty is to represent the activity of various ions in the film as their concentration as a first approximation. The concentration needs a volume term in its expression. This difficulty was experienced by various

authors (67,71,140) and they assumed the existence of a layer near the fibre-water interface which they termed as volume of the cellulose phase and divided the measured weight concentrations by this volume term. In our case, as the anodic film is produced under a standard set of conditions which is identical in all the experiments, it will not be unreasonable to assume that the volume of the film phase will be constant in all the cases. We can, therefore, assume that the effect of the volume term will be insignificant in the above representation and drop the term from the equation. We can thus express the activity of the dye in the film phase as a product of the concentration of the ions in the film

$$a_F = \left[Na_F^z\right] \cdot \left[C_F\right]$$

Hence

$$-\Delta\mu^o = zRT \ln\left[Na_F\right] + RT \ln\left[C_F\right] - zRT \ln\left[Na_B\right] - RT \ln\left[C_B\right]$$

We have assumed that the film possesses a positive charge and the dyes are completely ionised. The dye anion is attracted to the film as a result of the opposite nature of their charges. When the dye anion is sorbed it will partly or wholly neutralise the charge on the film at the sites where it is sorbed. When the charge on part of the film is thus neutralised, the Na^+ ions should be able to diffuse inside the film, but as they have no sites for their sorption they will lie loosely in the film volume. If the dye is pure and no other electrolyte is present in the solution, the concentration of the Na^+ ions in the volume outside and inside the film, it can be assumed, will be the same. In the above equation, therefore, the two terms

expressing concentrations of Na^+ ions cancel out each other and we get

$$-\Delta\mu^o = R\,T\,\ln[C_F] - R\,T\,\ln[C_B]$$

Now the change in standard free energy of a reaction is constant at constant temperature. Therefore

$$\ln[C_F] - \ln[C_B] = \text{constant}$$

of

$$\frac{[C_F]}{[C_B]} = \text{constant}$$

The points of an isotherm obtained by plotting the values of $[C_F]$ against $[C_B]$ at one temperature should, therefore, lie on a straight line passing through the origin. We find that this is the case in sorption isotherms of all the three dyes examined and shown in Figures 30,31 and 32. We have, however, drawn attention to the fact that in some cases the points tend to a sigmoid shape. Hanson, Neale and Stringfellow (140) found that adsorption of Chlorazol Sky Blue FF on cellophane in presence of increasing amounts of salt followed a sigmoid curve. They attributed this to the presence of carboxyl groups in the cellophane, which by dissociation increase the negative charge of the surface and thus increase the difficulty of dyeing. The reasons for sigmoid curves in the present case may similarly represent penetration difficulties experienced by the dye anions, but from a different cause. It may be that the dye anions on initial sorption decrease the surface charge progressively and thus the rest of the anions after the first will not have the same force of attraction with the result that their sorption becomes more difficult. The possibility that the

first anion sorbed will make the sorption of the next more difficult by blocking a pore of the film, in which we have assumed it diffuses, may also be a reason for the shape of the curves. It may be noticed that at higher temperature this tendency to sigmoid shape is not visible perhaps because the increased thermal agitation nullifies the effect of the blocking of the pores.

The affinity $(\Delta\mu^{o}_{(experimental)})$ of each dye has been calculated for each individual point of the sorption isotherm by means of the above equation. These results are given in Tables 20, 21 and 22. The tables also contain the values of $\frac{\Delta\mu^{o}}{RT}$ for all the points which will be utilised later for the calculation of heats of sorption. It will be observed that the affinities have a negative sign. We have seen that affinity is the change of standard free energy of a system. "The sign of the standard free energy gives an indication of whether the process is possible or not under these conditions; if the value is negative it means that the reaction with reactants and products in their standard states can take place at the particular temperature." (141) The above indicates that sorption of the dyes by the anodic film is a spontaneous process. This fact provides a check that the derivation of the equation, with the assumptions made to enable the calculation of such quantities as standard free energy, is not inherently wrong.

Table 20.

Affinity ($\Delta\mu^o$) in gm.cal.per mole for ORANGE I at 25°,40°,60°,80°C

25°C	-4540	-4490	-4560	-4700	-4770	Mean value -4610			
40°C	-4360	-4260	-4340	-4320	-4360	-4410	Mean value -4410		
60°C	-4160	-4030	-3820	-3880	-3860	-3900	-3870	-3920	Mean -3930
80°C	-3420	-3260	-3210	-3120	-3220	Mean value -3250			

Table 21.

Affinity ($\Delta\mu^o$) in gm.cal.per mole for ORANGE II at 25°,40°,60°,80°C

25°C	-4200	-3950	-3860	-3950	-3950	Mean -3960	
40°C	-3860	-3670	-3700	-3650	-3700	Mean -3720	
60°C	-3360	-3430	-3450	-3360	-3260	-3380	Mean -3375
80°C	-3270	-3210	-3180	-3200	-3120	Mean -3200	

Table 22.

Affinity ($\Delta\mu^0$) in gm.cal.per mole for AZO GERANINE 2G at 25°, 40°, 60° and 80°C

25°C	-3950	-3980	-3950	-3950	-3990	Mean	-3960
40°C	-3780	-3800	-3750	-3740	-3800	-3780	Mean -3780
60°C	-3650	-3580	-3480	-3550	-3550	-3540	Mean -3560
80°C	-3430	-3240	-3150	-3150	-3250	-3190	Mean -3230

The individual readings of affinity in the above tables are fairly constant and the deviation is not more than ± 200 gm.cal. approximately. Again, this deviation does not follow any particular trend and hence should be regarded as experimental error rather than indication of any peculiarity. As expected, the affinities vary with temperature. The mean value of affinity of each dye for a mean temperature of 50°C , which will represent its affinity for the anodic film, is shown in the following table.

Table 23.

The Mean affinity ($\Delta\mu^0$) of the dyes for a mean temperature of 50°C

ORANGE I	ORANGE II	AZO GERANINE 2G
-4050 gm.cal./mole	-3570 gm.cal./mole	-3630 gm.cal./mole

The next step in the thermodynamic treatment of the isotherms is to calculate the heats of reaction, which may provide clues to the mode of attachment of the dyes to the film. The standard heat of reaction may be defined as the heat absorbed when one mole of dye is sorbed on an undyed film from an infinitely dilute solution. The heat of reaction can be determined by measurements of the affinity at different temperatures by an equation which will be derived presently.

Differentiating $\frac{\Delta\mu^o}{T}$ with respect to temperature, we have,

$$\frac{d\,\frac{\Delta\mu^o}{T}}{d\,T} = \frac{1}{T}\cdot\frac{d(\Delta\mu^o)}{d\,T} + \Delta\mu^o\left(-\frac{1}{T^2}\right)$$

$$= \frac{1}{T}\cdot\frac{d(\Delta\mu^o)}{d\,T} - \frac{1}{T^2}\cdot\Delta\mu^o$$

Now $\Delta\mu^o = \Delta H^o - T\,\Delta S^o$. Substituting this, we obtain

$$\frac{d\left(\frac{\Delta\mu^o}{T}\right)}{d\,T} = \frac{1}{T}\cdot\frac{d(\Delta\mu^o)}{d\,T} - \frac{1}{T^2}(\Delta H^o - T\,\Delta S^o)$$

$$= \frac{1}{T}\cdot\frac{d(\Delta\mu^o)}{d\,T} - \frac{\Delta H^o}{T^2} + \frac{1}{T}\cdot\Delta S^o$$

Again $\Delta S^o = -\frac{d(\Delta\mu^o)}{d\,T}$

Hence

$$\frac{d\left(\frac{\Delta\mu^{o}}{T}\right)}{dT} = -\frac{\Delta H^{o}}{T^{2}}$$

If H^{o} is taken as constant over a small range of temperature, integration of the above equation will give

$$\frac{\Delta\mu^{o}}{T} = \frac{\Delta H^{o}}{T} + \text{constant}$$

and dividing by R , the gas constant ,

$$\frac{\Delta\mu^{o}}{RT} = \frac{\Delta H^{o}}{RT} + \text{constant}$$

Thus if the values of $\frac{\Delta\mu^{o}}{RT}$ are plotted against $\frac{1}{T}$, a straight line should result and the slope of the line would be $\frac{\Delta H}{R}$ (dropping subscript to make it general) from which the heats of reaction can be calculated. The mean values of $\frac{\Delta\mu^{o}}{RT}$ at each of the four temperatures for each dye shown in Table 24 were plotted against the reciprocal of the respective temperature, in Figures 37 and 38 and the slope determined. The bottom line shows the values of heats of reaction obtained from the slopes. These values of heats of reaction are mean for the whole temperature range considered, and therefore the mean temperature is also shown against the column.

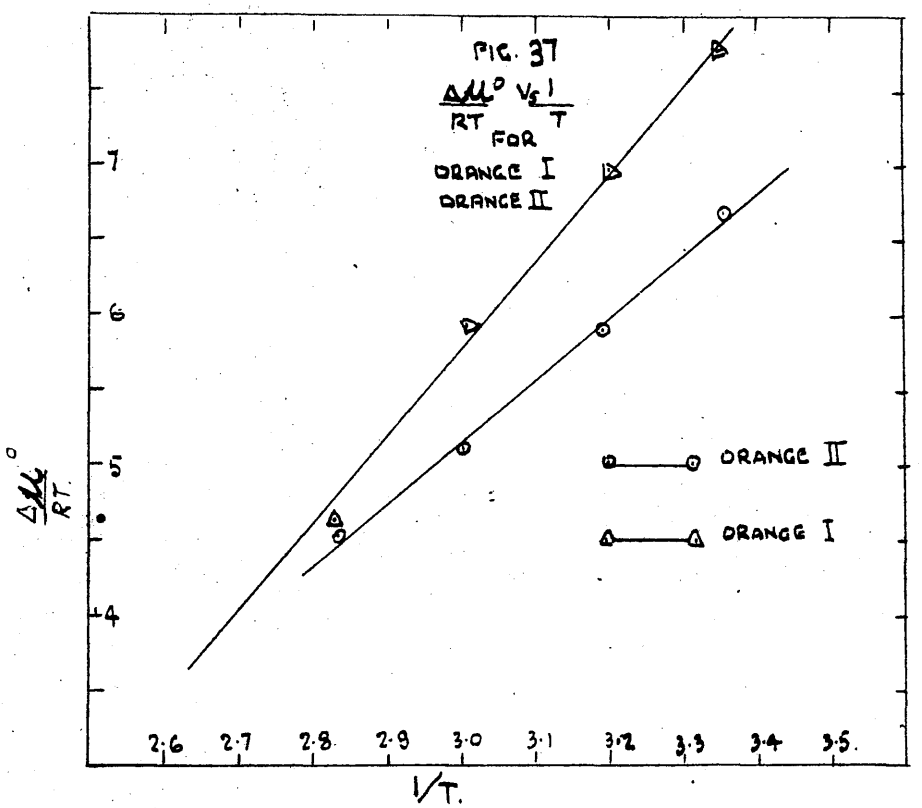


FIG. 37
$\frac{\Delta\mu^\circ}{RT}$ Vs $\frac{1}{T}$
FOR
ORANGE I
ORANGE II
ORANGE II
ORANGE I
$\frac{\Delta\mu^\circ}{RT}$
7
6
5
4
2·6 2·7 2·8 2·9 3·0 3·1 3·2 3·3 3·4 3·5.
1/T.

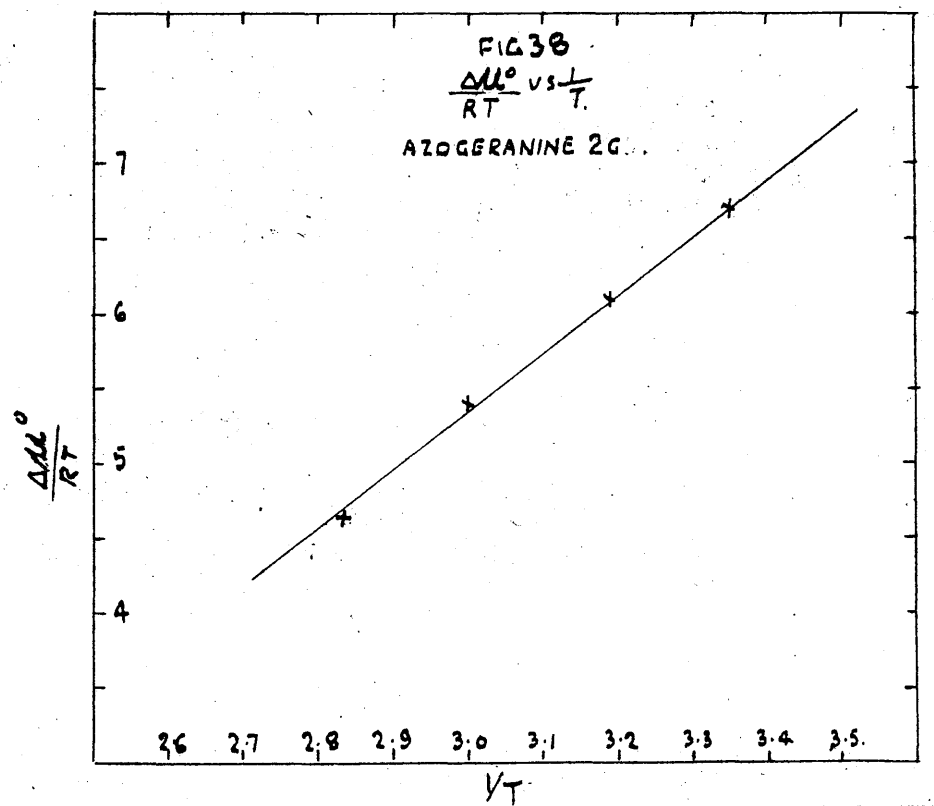


FIG 38
$\frac{\Delta\mu^\circ}{RT}$ vs $\frac{1}{T}$.
AZOGERANINE 2G..
$\frac{\Delta\mu^\circ}{RT}$
7
6
5
4
2,6 2,7 2,8 2,9 3·0 3·1 3·2 3·3 3·4 3·5.
1/T

Table 24.

Mean values of $\frac{\Delta\mu^o}{RT}$ and heats of reaction for the dyes at 25°, 40°, 60° and 80°C.

Temp.	$\frac{1}{T(\text{abso.})} \times 10^3$	Mean values of $\frac{\Delta\mu^o}{RT}$ and heats of reaction (bottom line)		
		Orange I	Orange II	Azo Geranine 2G
25°C	3.356	-7.76	-6.72	-6.71
40°C	3.195	-6.98	-5.91	-6.09
60°C	3.003	-5.94	-5.12	-5.39
80°C	2.833	-4.62	-4.57	-4.62
50°C	---	-11,800	-7,800	-8,000

It has been assumed during these calculations that the heats of reaction remain constant within the temperature range considered. It is known that they do so within small ranges. It will be interesting, therefore, to see how far this assumption is correct. This can be done by employing a form of Van't Hoff's equation. The equation is

$$\log \frac{C_{B_1}}{C_{B_2}} = \frac{\Delta H}{4.578} \frac{T_2 - T_1}{T_1 T_2}$$

where C_{B_1} and C_{B_2} are the concentrations of dye in solution for the same concentration of dye on the film at two temperatures T_1 and T_2.

We can calculate the heat of reaction (Δ H) of a dye within a range of two temperatures by means of this equation from the isotherms of the dye. This was done in the case of Orange I from Figure 30. Several values of the amount of dye on the film (C_F) were taken and ΔH calculated from the corresponding values of C_{B_1} and C_{B_2} at two temperatures. The values did not differ very much. The mean value for each temperature range is shown in Table 25.

Table 25.

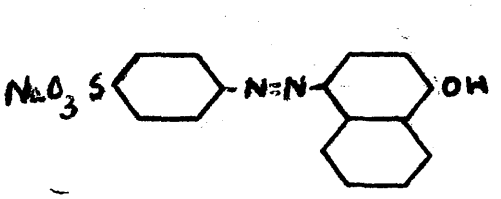
Mean values of heats of reaction (-Δ H) of Orange I in cal./mole.

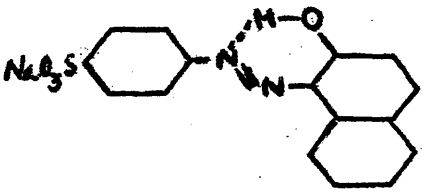
When the temperatures (T_1 and T_2) are					
25°C and 40°C	25°C and 60°C	25°C and 80°C	40°C and 60°C	40°C and 80°C	60°C and 80°C
-11,800	-11,900	-12,600	-12,200	-13,100	-14,600

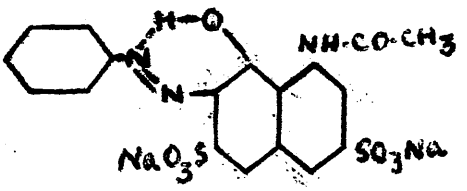
This shows that the heat values are quite uniform over lower ranges of temperature. At higher temperatures, they tend to increase. The fact that within a small range of temperature the heats of reaction at all points of the isotherm are fairly constant indicates that probably all the sites in the film are of the same nature and at equilibrium a unimolecular layer of dye molecules is formed on the film. This conforms with Langmuir's conception of adsorption, but we have seen that the Langmuir formula does not apply to the isotherms. This shows that the mechanism of sorption is more complex than the simple mechanism postulated by the Langmuir theory. By comparing the isotherms obtained in the case of these dyes with the classified isotherms in Figure 33 it was shown that the isotherms do not represent adsorption of any kind, but solution of dye in the film. It is difficult to say anything more than this.

The energy changes involved in the sorption of dye by the film depend only upon the state of the dye-film system and hence should be indicative of the trends in the system. Accordingly, the mean values of affinities of the three dyes considered as shown in Table 23 should represent their affinity for the film. This shows that Orange I has the greatest affinity for the film while Orange II and Azo Geranine 2G have about the same affinity. This may be due to the fact that Orange I has a hydroxyl group para to the azo group and consequently it is free, while in Orange II and Azo Geranine 2G the hydroxy groups are bonded, as

shown below.



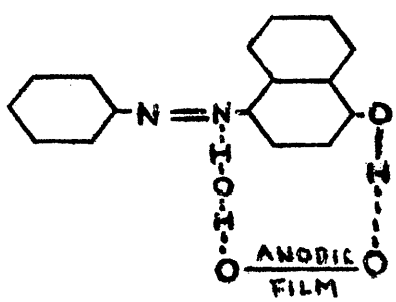




Orange I, therefore, may be more easily sorbed by the formation of a hydrogen bond between the oxygen atoms of the hydroxyl and the aluminium oxide of the film. It appears that with Orange II and Azo Geranine 2G bonds may not be as easily formed, which perhaps is demonstrated in their lower affinity figure.

The heat of reaction represents the number and energy of the bonds formed between the dye and the film. From the results in Table 24, it appears that two or even three hydrogen bonds may be involved in the case of Orange I while in the case of Orange II and Azo Geranine 2G, it may be either one or two. It is very difficult to judge precisely the number of bonds from

the values of heats of reaction because the values obtained for similar bonds in many other cases are widely varying. Again the present knowledge of the hydrogen-bond forming powers of the various reactive groups in the dye is quite inadequate for predicting heats of reaction, especially in view of the fact that the energies of such bonds appear to vary with the nature of the participating groups. Orange I can form a hydrogen bond, as mentioned, with the film through its hydroxyl group, but this will be one hydrogen bond whose heat of reaction may be 5 - 8 K cal.per mole(108). The actual value obtained (12 K cal.per mole) (Table 24) is much larger than this. There is no possibility of any other point of direct attachment between the dye molecule and the film as neither of them has a hydrogen atom to bond the two. It is, therefore, suggested that a water molecule forms a bridge between a nitrogen atom of the azo group and another oxygen of the aluminium oxide of the film, as shown below



This will, of course, involve three hydrogen bonds and the total energy value obtained appears lower than the range in which it should lie if values for similar bonds reported in the literature are taken into account. We should take into consideration,

again, that no definite knowledge of these values is available and therefore we have to base our assumptions upon a limited available set of data. One of the bonds is a N·····H - O bond and this has usually a low bond energy. It would not be unreasonable, therefore, to assume that the magnitude of the heats of reaction obtained indicates three hydrogen bonds as shown.

Orange II and Azo Geranine 2G have no free hydrogen atom which could form a bond. (We assume here, of course, that aluminium oxide of the film also does not have a proton. This will be discussed later.p.166) We can, therefore, say that unless the existing bond (N·····H - O) breaks, the only possible attachment may be said to be through a water molecule something like shown above. It is mentioned earlier in the introduction that because of the smaller magnitude of the energies involved in hydrogen bond formation, particularly in a N·····H - O bond like this, it should be easy to disrupt a hydrogen bond; but it is not known under what circumstances it is disrupted. If, for a moment, we assume that the existing bond is broken, the dye molecule will have a similar structure to that of Orange I so far as attachment through hydrogen bond to the film is concerned. It should then form three bonds, as suggested above. The smaller magnitude of the heat involved may be due to opposite nature of the heat of disruption of the existing bond. This would, then, indicate that fastness with which all the three dyes are attached to the film will be similar. An

experiment to desorb the dyed foils should, therefore, prove interesting.

Desorption of Orange I , Orange II and Azo Geranine 2G

Desorption experiments are generally carried out at the temperature at which sorption is done. In the present case, as the anomalous behaviour of water towards the film at higher temperatures was known, the foils dyed at low temperature were desorbed at the corresponding temperatures by putting them in 50 ml. of distilled water for a period 50 per cent. longer than the time taken to attain equilibrium during sorption. It is not known whether the equilibrium was established; but the results which are contained in Table 26 should be regarded rather as qualitative than quantitative. They are only meant to be comparative and to indicate the fastness as such of the dye on the film. The dyed strips with lowest sorption of dyes were also desorbed, but the amount desorbed was so low that it could not be estimated by the Spekker Absorptiometer. It should also be mentioned that the amounts of desorbed dye were very low in other cases as well, and the Spekker readings were near the range where they would not be reliable. However, as mentioned, these readings should be considered as merely qualitative.

Table 26.

Desorption of Orange I , Orange II and Azo Geranine 2G from dyed films at 25° and 40°C.

Temp.	Orange I millimoles/Kgm.			Orange II millimoles/Kgm.		
	original dye	amount desorbed	% dye desorbed	original dye	amount desorbed	% dye desorbed
25°C	986.0	47.3	4.8	408.0	51.2	12.5
	442.0	21.7	4.9	255.0	29.3	11.4
40°C	1020.0	43.2	4.2	340.0	44.9	13.1
	816.0	33.7	4.1	238.0	24.7	10.3

Temp.	Azo Geranium 2G millimoles/Kgm.		
	original dye	amount desorbed	% dye desorbed
25°C	98.3	14.3	14.5
	70.2	10.2	14.5
40°C	126.3	16.8	13.4
	60.9	8.2	13.5

The results indicate that Orange I is faster than both Orange II and Azo Geranine 2G. It will also be noticed that, in general, percentage dye desorbed at higher temperature ($40^{o}C$) is less than that at $25^{o}C$. This is probably in accordance with the fact that treatment with water "seals" the film and the higher the temperature, the greater is this sealing.

Considering the results from the point of view of attachment of the dye to the film by hydrogen bonds, it appears reasonable to suppose that Orange I will have more points of attachment to the film than Orange II and Azo Geranine 2G. This gives support to the view that in the two latter dyes, the existing hydrogen bond is not disrupted, but they are attached to the film through a bridge of water molecule.

Consideration of entropy changes involved in the process of dyeing the film may prove useful at this point. We know the change of standard free energy and the change of heat content during the process and we can calculate the entropy change from the formula -

$$\Delta \mu^{o} = \Delta H^{o} - T \Delta S^{o}$$

$$\text{or } -\Delta S^{o} = \frac{\Delta \mu^{o} - \Delta H^{o}}{T}$$

Table 27 contains the mean heats of reaction and the entropy changes calculated at the mean temperature of $50^{o}C$. The mean standard free energy changes have been taken as given in Table 23

Table 27.

Mean values of the heats of reaction (ΔH) and entropy changes (ΔS) of the dyes for a mean temperature of 50°C.

Dye	$-\Delta H$ Kgm.cal.per mole	$-\Delta S$ gm.cal.per °K per mole
Orange I	12	25
Orange II	8	14
Azo Geranine 2G	8	13

Even though the thermodynamic function "entropy" has been known for a long time, the actual entropy of a system is not easily defined. However it can be said that like all the other energy functions, entropy is also a property of a system or a substance dependent only upon its state, although it being an extension property, the amount of the substance enters into its calculation. A precise physical significance of entropy cannot be easily given. Though consideration of entropy changes may give us an indication that the process is reversible or irreversible (spontaneous) or that there is an increase of "disorder" or "chaos", this information does not appear to be of immediate significance when considering chemical

reactions. Similarly the statistical approach to entropy and maximum probability also does not help to clear the picture. The contribution of entropy change data to the understanding of restriction of vibrational, rotational and translational movement of molecules or their parts may be significant. The actual entropy of a system or a molecule is made up of the sum of these entropies of its parts. When a change in the system takes place and these motions are restrained, the entropy of the system increases. The increase in entropy changes observed in the present case as shown in Table 27 may signify restraint upon the motion of dye molecules as a result of their attachment to the film. In that case, it is obvious that the greater the number of points of attachment, the greater will be this restraint upon their motion. Table 27 shows that the value of the entropy change of Orange I is the largest, while those of Orange II and Azo Geranine 2G are about the same. This supports the suggestion made above that Orange I has two points of attachment (three hydrogen bonds) to the film while Orange II and Azo Geranine 2G, each have one (two hydrogen bonds).

If we assume that the attachment of dye molecules to the film is through hydrogen bonds, the attachment should not be of a very strong nature, as the energy of such bonds is low. It has been mentioned in the introduction that it is the ease with which a hydrogen bond can be formed or ruptured that makes this bond such an important one in chemistry. It should, therefore, have been possible to desorb the dye completely from the film.

The direct dyes which are attached to cellulose by hydrogen bonds can be desorbed almost completely. It was, however, observed in the present case, that no treatment whatever could desorb the dye completely from the film without destroying the dye or the film. It will be observed from the Table 27 that even after such a prolonged treatment only 4 - 15% of the dye comes off the film. It is very difficult to explain this behaviour. It may be that the film consists of a large number of active basic sites to which dye anions are strongly attached. It may be difficult to remove dye molecules from these sites. A similar observation was made in the case of cotton cellulose. Gnehm and Kauffler (72) found that the last traces of dye adsorbed by cotton are very difficult to wash out, even by repeated water washings. Peters and Vickerstaff (71) observed that the experimental points of a curve representing the adsorption isotherm of Benzopurpurin 4B on cotton in the absence of any foreign electrolyte lie on a straight line intercepting the fibre axis. They explain this on the assumption that the cotton cellulose contains a few basic sites which take up the dye strongly even in the absence of electrolyte, but when all such sites are saturated the dyeing proceeds on less active sites, which are large in number. The behaviour of water towards the film, which has been frequently mentioned, may be another factor involved. As the periods required to attain equilibrium sorption are long, it may happen that after the dye is sorbed the water will have had a "sealing" effect. This "sealing" effect is achieved within a short time by hot or boiling water.

It is likely that water at lower temperatures also will have some effect on the structure of the film, affecting sorption and desorption of the dye. The desorption bath of distilled water may itself have some similar effect on the film. Very little is known about the porous structure of the film. It may be that after the dye molecule has diffused inside the pores, it is difficult to diffuse out again. One or many of these factors may be playing a part, resulting in the firm fixation of the dye molecule.

The affinities which we have considered earlier are the affinities, as a whole, of the reaction measured when it has attained equilibrium. To predict the dyeing behaviour of a dye, we should know the affinity at the start of the reaction. One way in which the relative affinities of dyes may be expected to become manifest is in the sorption of the dye in the initial stages of the dyeing process. It is evident that the dye having the greatest difference in chemical potential between the film and the solution will be most quickly sorbed. It should be noted here that this difference in chemical potential is not the standard difference in chemical potential which we have determined earlier, and which refers to the difference between the film and the solution both of which contain the dye in the standard state of unit activity determined at equilibrium. The relative affinity - the change in chemical potential - when the film-dye system is not in equilibrium is given by the equation

$$-\Delta\mu = \Delta\mu^{o} + RT \ln a_{F} - RT \ln a_{B}$$

Since we are considering the chemical potential difference at the start of the process, there will be no dye in the film. The film term may, therefore, be dropped, as it will be the same for all dyes. Therefore, we get,

$$-\Delta\mu = \Delta\mu^{o} - R\,T\,\ln a_{B}$$

Representing the activity of dye in solution by ionic concentrations as the solutions are very dilute, we get

$$-\Delta\mu = \Delta\mu^{o} - Z\,R\,T\,\ln\left[Na_{B}\right] - R\,T\,\ln\left[C_{B}\right]$$

Now, if the dye is pure and there is no foreign electrolyte present,

$$\left[Na_{B}\right] = Z\left[C_{B}\right]$$

Substituting, we get

$$-\Delta\mu = \Delta\mu^{o} - (Z+1)\,R\,T\,\ln\left[C_{B}\right]$$

As we know the mean values of the standard chemical potential difference from the Table 23 , we can calculate the relative affinities from this equation for an initial concentration of dye. The following table contains the affinities for the undyed film from dyebaths containing 0.30 and 3.0 moles of dye per litre. This is the range of concentration used in the experimental work described earlier and generally used in practice.

Table 28.

Relative Affinities of Dyes for Undyed Film.

	order of $\Delta\mu^{o}$
Orange I	-4.03 k.cal.
Orange II	-3.56 k.cal.
Azo Geranine 2G	-3.63 k.cal.

order of $\Delta\mu$ in 0.3 moles/litre dye		order of $\Delta\mu$ in 3.0 moles/litre dye	
Orange I	-0.45 k.cal.	Azo Geranine 2G	-5.74 k.cal.
Orange II	+0.01 k.cal.	Orange I	-5.44 k.cal.
Azo Geranine 2G	+1.73 k.cal.	Orange II	-4.97 k.cal.

It will be observed that the order in dyeing differs from the order of standard affinities in the case of higher concentrations, although the order between Orange I and Orange II, dyes having the same ionic charge, remains unchanged. The dyes will be sorbed on the film by virtue of their affinity, and this will be manifest when a mixture of dyes having different affinities is used. If mixtures of two or more dyes are used and if they have different affinities, the dyeing of the film will show a changing shade as the dyeing proceeds. Of course, at equilibrium the shade will always be the same, but dyeing is very rarely carried on in practice for such long periods. Peters and

Vickerstaff (71) observed a similar effect in the case of viscose rayon. They studied the effect of concentration of a foreign electrolyte in the bath while dyeing viscose with direct dyes, but even in the absence of a foreign electrolyte, similar effects may be observed.

The study of sorption equilibrium has brought out the following points:-

(1) The nature of the isotherms suggests that the sorption may be representing solution of dye in the film; it is not a case of a Langmuir type adsorption.

(2) Standard affinities calculated by the thermodynamic treatment indicate the order, Orange I > Orange II > Azo Geranine 2G.

(3) The calculation of heats of reaction shows that probably three hydrogen bonds are involved in the case of Orange I and two in the case of Orange II and Azo Geranine 2G. The possible linking in all the cases has been indicated. It is likely that Orange II and Azo Geranine 2G are linked to the anodic film through a water molecule.

(4) The entropy change calculations show that the greater entropy change in Orange I, as compared with Orange II and Azo Geranine 2G is probably an indication of the restricted rotational and translational motion of the dye molecules, due to more points of attachment to the film being involved.

(5) Relative affinities of the dye for undyed film at the start of the process have been calculated. These show that the dyeing order could change with different concentrations of dyes if they have different ionic charges. The order will not be affected, however, if dyes with the same ionic charges were involved. The knowledge of these affinities may be useful in practical work.

C. Simple Organic Compounds.

The experiments described in the preceding pages have indicated that the dye molecules are probably attached to the anodic film by means of hydrogen bonds. To obtain supporting evidence for the suggestions made earlier, it was thought best to try simple organic compounds to avoid the complications involved by the simultaneous presence of several possible active groups in each molecule.

It was pointed out in the introduction that it is not possible to obtain indirect confirmatory evidence like infra red spectral curves, in the case of dyed film or fibres. We have, therefore, to depend upon physico-chemical calculations of bond energies. The possibility of hydrogen bond formation can be judged by an indirect method. If two compounds such as phenol and o-nitrophenol are sorbed on the anodic film, then if the mechanism of sorption is by a hydrogen bond, phenol should be taken up while o-nitrophenol should not be, on account of its internal bond. Marsden and Urquhart (92) tried these two compounds on cellulose acetate and found that phenol is sorbed and o-nitrophenol is not. They suggested, therefore, that the mechanism is hydrogen-bond formation. We have also tried both these compounds and the results are described in the following pages.

To obtain information about the part played by different groups in a simple dye molecule, like Orange I or Orange II , other simple compounds including benzeneazo- α -naphthol ,

benzeneazo-ß-naphthol, benzene sulphonic acid and azobenzene were tried. The results obtained generally support the conclusions described above.

1. Phenol and o-nitrophenol.

Solutions of phenol and o-nitrophenol were prepared by dissolving 1.0 gm. of 'Analar' quality compounds in a litre of distilled water. Various amounts of this solution were diluted to 50 ml. to give baths containing different initial concentrations of each compound. Sorption of the two compounds on the anodic film at 40° and $60^{\circ}C$ was carried out for 48 hours, which was sufficient for the attainment of equilibrium. Phenol in the baths left behind after sorption was estimated by the bromine method, while o-nitrophenol was estimated by using ultraviolet light in the Spekker Photoelectric Absorptiometer. The results obtained in the case of phenol are tabulated below and plotted in Figure 39.

The o-nitrophenol readings on the absorptiometer showed that this compound is not sorbed at all.

The sorption isotherms of phenol drawn in Figure 39 are again straight lines passing through the origin, and show that the sorption mechanism is of a nature similar to the dyes considered in the previous section. Heats of reaction can be calculated from the isotherms with the help of the equation

$$\log \frac{C_1}{C_2} = \frac{\Delta H}{4.578} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where C_1 and C_2 are concentrations in solution in equilibrium with the same amount of phenol sorbed at temperature T_1 and T_2 on the absolute scale, and ΔH is the heat of reaction

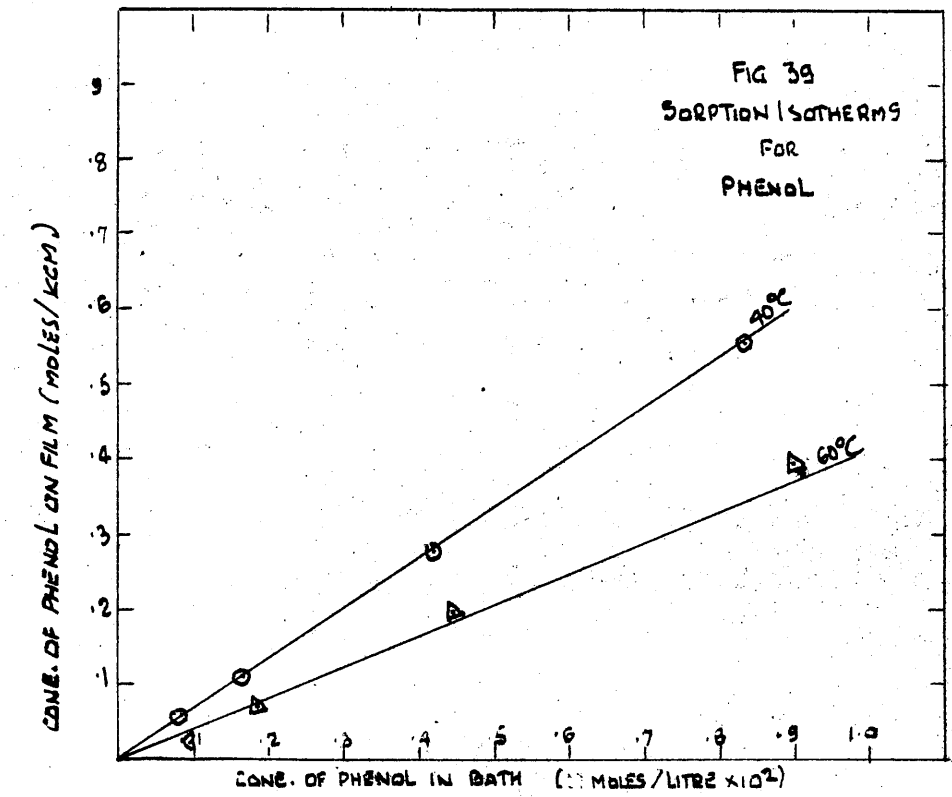


FIG 39
SORPTION ISOTHERMS
FOR
PHENOL
40°C
60°C
CONC. OF PHENOL ON FILM (MOLES/KGM)
CONC. OF PHENOL IN BATH (MOLES/LITRE ×10²)

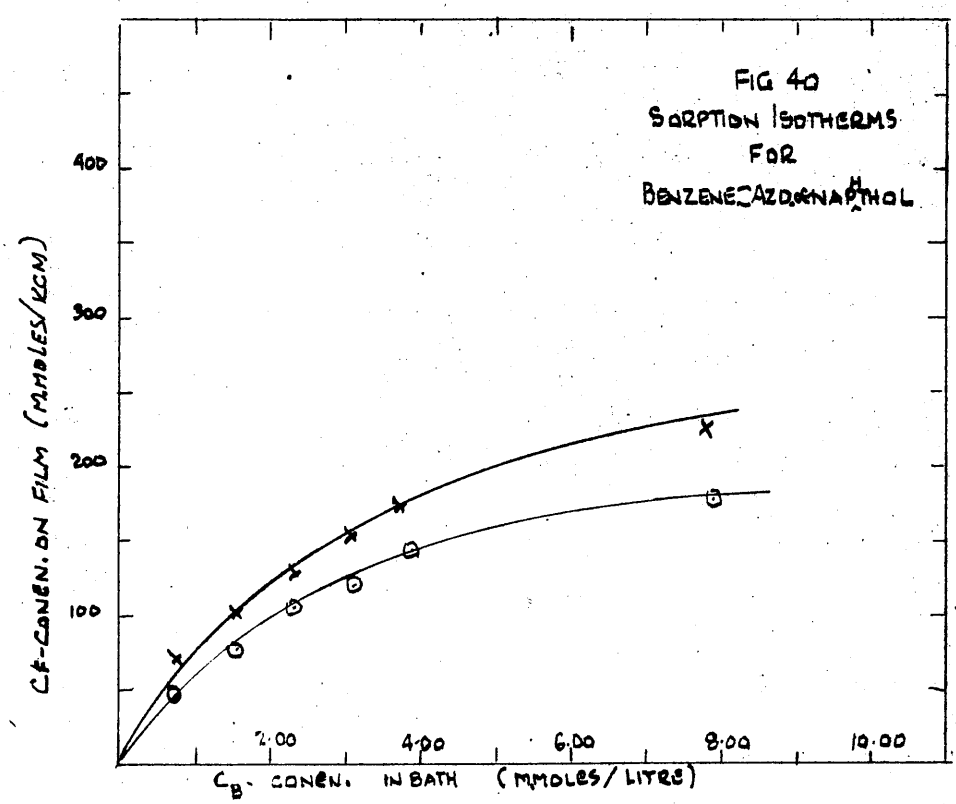


FIG 40
SORPTION ISOTHERMS
FOR
BENZENE-AZO-α-NAPHTHOL
CE-CONCN. ON FILM (MMOLES/KGM)
CB- CONCN. IN BATH (MMOLES/LITRE)

Table 29.

Equilibrium Sorptions of Phenol at 40° and 60°C.

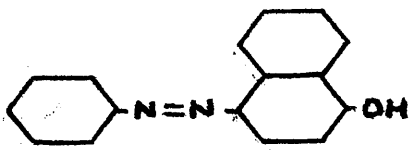
Temp.	40°C		60°C	
Initial concn. in gm/litre	Amount of phenol sorbed (moles/Kgm)	Phenol left in bath (moles/litre)	Amount of phenol SORbed (moles/Kgm)	Phenol left in bath (moles/litre)
1.0	0.5537	0.008316	0.3955	0.008978
0.5	0.2787	0.004160	0.1976	0.004459
0.2	0.1108	0.001663	0.07112	0.001830
0.05	0.0537	0.0008316	0.01576	0.0009977

The average heat of reaction derived from the above equation is of the order of -5 K.cal.per gm.mole. This indicates that phenol is attached to the film by one hydrogen bond. The fact that phenol is taken up, and o-nitrophenol is not, is in itself a definite indication that hydrogen bond formation is involved. Calculation of heat of sorption of phenol on cellulose acetate led Marsden and Urquhart (92) to quote a figure of approximately 2 - 3 K.cal.per gm.mole , which is lower than the bond energy of a hydrogen bond. However, they considered that the sorption of

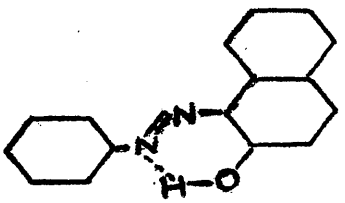
phenol and p-nitrophenol, and the non-sorption of o-nitrophenol, is a sufficient indication of hydrogen bond formation in the former. In our case these two results give strong support to the theory of hydrogen bond formation in the anodic film, though of course, we are conscious of the fact that calculation of heats of reaction based on two temperatures only, should not be taken as completely reliable.

2. Benzeneazo-∝-naphthol and Benzeneazo-ß-naphthol.

Benzeneazo- -naphthol and benzeneazo-ß-naphthol, which are the respective unsulphonated, water-insoluble, forms of Orange I and II, were selected. Benzeneazo-∝-naphthol has a free hydroxyl group which can take part in hydrogen-bond formation, while the similar group in benzeneazo-ß-naphthol, being ortho to the azo group, is involved in a six-membered ring through an internal hydrogen bond:-



Benzeneazo-∝-naphthol



Benzeneazo-ß-naphthol

In the preceding section we have suggested that Orange II is attached to the anodic film through a bridge formed by a water molecule, by means of two hydrogen bonds. If this remains true

in the present instance, benzeneazo-α-naphthol should be taken up, but the ß-naphthol analogue should not be sorbed.

Solutions of the two compounds were prepared by dissolving 2.0 gm. of pure sample in a litre of dry 'Analar' benzene. First, a few ml. of benzene were distilled and the remainder kept over dry calcium chloride to ensure absence of moisture. The various amounts of each solution were diluted to 50 ml. with benzene added by means of an automatic burette designed and constructed by the author. This burette, shown in Figure 42, is completely closed and air enters after passing through calcium chloride tubes. Thus complete exclusion of moisture was ensured. Quick-fit test-tubes with hooks and springs were used to hold the treating baths. The sorptions at 40° and $60^{\circ}C$ were allowed to continue for 48 and 24 hours respectively, which was by previous rate studies, found to be adequate for attaining equilibrium. The concentrations of solution of benzeneazo-α-naphthol were estimated on the absorptiometer using ordinary light, while ultra-violet light was used in the case of benzeneazo-ß-naphthol . The results of the experiments with benzeneazo-α-naphthol are tabulated in Table 30.

Table 30.

Equilibrium Sorption of Benzeneazo- ∝ -naphthol at 40° and 60°C

a = concn. of benzeneazo-∝-naphthol on the film in millimoles per Kgm. dry film.

b = concn. of benzeneazo-∝-naphthol in solution in millimoles per litre.

40°C	a 72.0	100.8	129.6	153.6	172.7	225.0
	b 0.745	1.57	2.31	3.08	3.78	7.85
60°C	a 48.0	76.8	105.6	120.0	144.0	177.5
	b 0.766	1.55	2.33	3.12	3.91	7.89

The isotherms are plotted in Figure 40.

Benzeneazo-ß-naphthol was not sorbed at all. This supported the conclusions reached earlier. The results of sorption of benzeneazo-∝-naphthol suggest the following:-

(i) The amount sorbed is very small in each case as compared with Orange I. We consider this due to the non-polar nature of the solvent. Both the anodic film and the dye itself will be electrically uncharged and consequently there will be no attraction between them. Therefore sorption will take place less readily and the driving force causing diffusion inwards will be correspondingly reduced.

(ii) The isotherms are curves of the type (d) of Figure 33 which represent adsorption of Langmuir type and not like the straight lines that were obtained earlier. This is probably due to the nature of adsorption of benzeneazo-α-naphthol, the molecules being attached only to layers near the surface. The isotherms when plotted according to the Langmuir equation derived on page 122 give straight lines (Figure 41). The fact that a straight line is obtained is not of course a definite evidence of Langmuir adsorption. The reciprocal of the intercept of both the lines on the film axis will give the value of the constant C_M, which, as mentioned, represents the surface area of the film and changes slightly with temperature. The intercept of both the Langmuir lines should, therefore, be approximately the same in our case because there is no likelihood of a great change in the effective surface area. This is found to be the case in Figure 41. One point representing the lowest concentration lies away from the straight line in each case, but still it is not unreasonable to take the Langmuir fit as good. It may be argued that Langmuir adsorptions are not always so small in amount as in this instance. The Langmuir adsorption would naturally depend upon the nature of the adsorbent. The anodic film has narrow, long, pores and in the absence of any driving force, it may be supposed that the sorption virtually stops after the blocking of the pores by the first adsorbed surface layer. If we take the diameter of the pores as something in the region of 10 Å, the molecule of benzeneazo-α-naphthol will have a similar diameter and it can

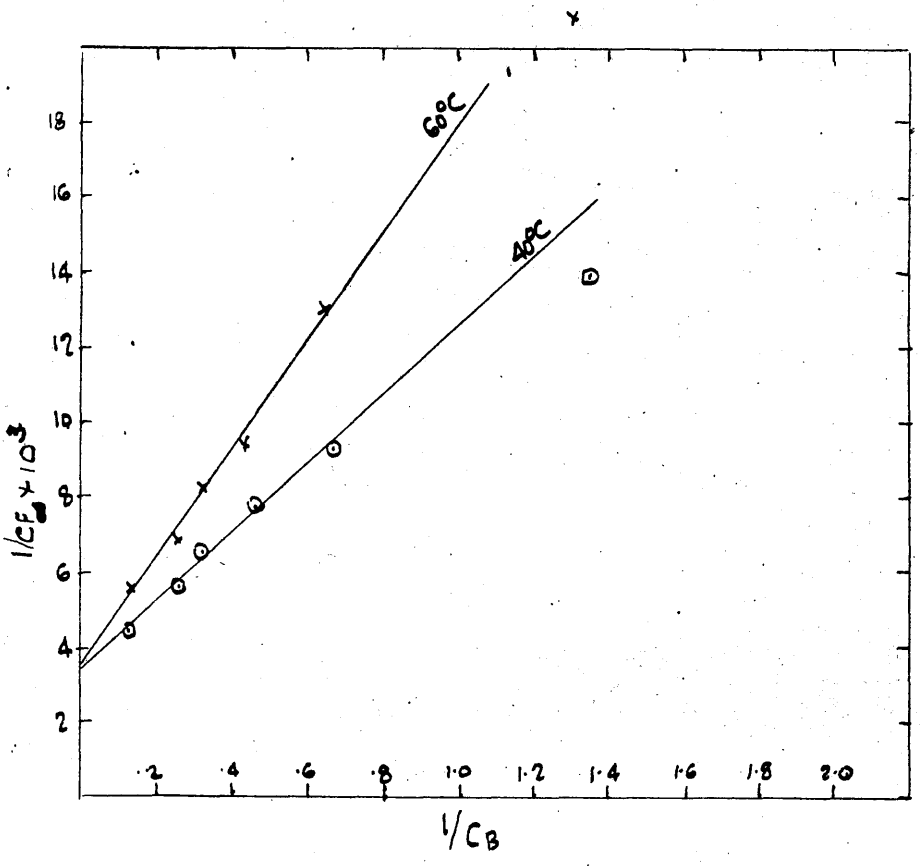


FIG 41

ABSORPTION ISOTHERMS

BENZENE — AZO-α-NAPHTHOL

LANGMUIR BASIS

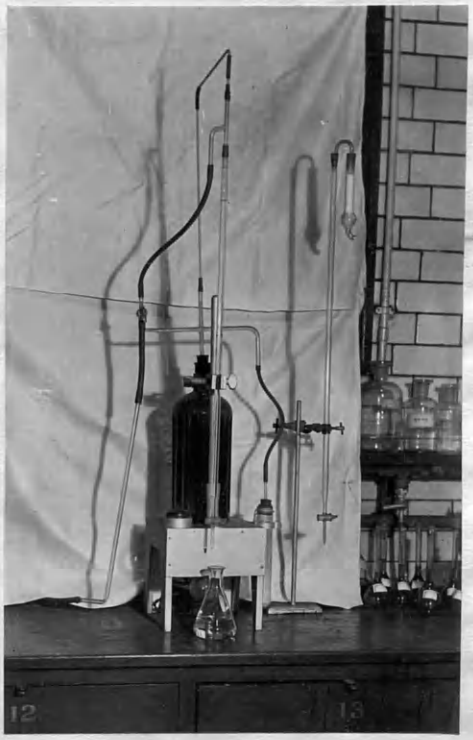


Fig. 42. Automatic Burette.

thus effectively block the pores. Nothing definite can be said about the nature of the binding force between the film and the adsorbed molecules. The above considerations show that van der Waals forces may be involved, but the calculation of heat of reaction from the isotherms by the equation on page 132 leads to a value of 4.0 K.cal.per gm.mole . This would indicate that one hydrogen-bond is involved. Examples of the formation of hydrogen bonds between molecules in solvents like benzene and carbon tetrachloride are known (108); for example Benzoic acid is associated to double molecules in such solvents and the value of 4.3 K.cal.per gm.mole has been found as the hydrogen bond energy. The attachment of the benzeneazo-∝-naphthol molecules to the anodic film through a hydrogen bond appears, therefore, more likely.

An experiment was done to sorb benzeneazo-ß-naphthol from 50% aqueous alcohol solution. This should have been sorbed if the suggestion that water molecules form a bridge between the film and the dye molecules holds true in this instance, but it was found that the dye was not sorbed at all. This could not be explained. Chipalkatti (142) found that the same dye is also not sorbed on wool from aqueous alcohol solution even after boiling for a considerable time. These facts seem to suggest that the unbonded nitrogen atom of the azo group is less able to form an external hydrogen bond in the unsulphonated than in the sulphonated dye. They also indicate that the hydrogen bond between the hydroxyl and the pure azo nitrogen is not ruptured, which was suggested as a possibility while discussing sorption of

Orange II by the film.(See p.139)

(iii) Azobenzene.

Impure azobenzene was crystallised thrice from pure alcohol and dried over vacuum. A solution in dry 'Analar' benzene was prepared by dissolving 0.125 gm. of this pure azobenzene in 250 ml. of dry benzene. A starting bath was made up of 10 ml. of this solution and 40 ml. of dry benzene, and various anodised strips were put in the bath for different periods of time from 1 hour to 48 hours. The baths were then examined on the absorptiometer using ultraviolet light. It was found that no sorption had taken place from any of the solutions.

An aqueous alcoholic solution of azobenzene was prepared by dissolving 1.0 gm. of pure substance in one litre of 50% aqueous alcohol. Various experiments were done to study the sorption of azobenzene from this solvent, using the same initial concentration and different periods of sorption and different initial concentration, for 48 hours at both 40° and 60°C. The baths after sorption were estimated on the absorptiometer as before, using ultraviolet light. The results so obtained are given in Table 31.

Table 31.

Sorption of azobenzene from aqueous alcoholic solution at 40° and 60°C.

Initial concn. of azobenzene in millimoles/Ltre.	Temperature °C	Time of sorption in hours	Amount sorbed on film in millimoles/Kgm.
0.55	40°C	8	131.0
0.55	40°C	16	183.4
0.55	40°C	24	196.5
0.55	40°C	48	393.0
5.50	40°C	48	524.0
4.40	40°C	48	917.0
3.30	40°C	48	131.0
2.20	40°C	48	524.0
1.10	40°C	48	262.0
5.50	60°C	24	1048.0
4.40	60°C	24	655.0
3.30	60°C	24	458.0

It is clear from the Table that the sorption of azobenzene from the solutions was very erratic. It is very difficult to explain this. We cannot, therefore, base any conclusion on the results However, the experiment does at least indicate that azobenzene is sorbed from the aqueous alcohol solution because so many results cannot be regarded as accidental. This sorption, together with the non-sorption from dry benzene solution, gives support to the water-bridge hypothesis in this particular case.

(iv) Benzene sulphonic acid and its sodium salt:-

After studying the effect of the azo and hydroxy groups in the molecules of Orange I and Orange II on the sorption on anodic film, the sorption of benzene sulphonic acid and its sodium salt were studied. The dyes are sodium salts, and hence the sodium salt of benzene sulphonic acid was first studied. Experiments to sorb this from aqueous solutions of the 'Analar' salt showed that it was not taken up at all. Six different readings were taken. The sodium salt was converted to acid by passing it through " H^+ cycle " zeolite and then titrating against $\frac{N}{100}$ sodium hydroxide solution with every precaution to prevent interference from atmospheric carbon dioxide. The process has been described in detail in the section "Technique and Methods" (Part II Section I) . This showed that the sodium sulphonate group did not play any part in the sorption of the dyes - Orange I and Orange II.

For experiments on sorption of the free acid, a 2.0 gm.per litre

solution was made by diluting 6.25 c.c. of a 32 percent. w/v solution of the acid as supplied by Messrs. British Drug Houses Ltd., to one litre, with distilled water. Sorption at 40°C for different periods from half an hour to 48 hours was carried out from a 50 ml. bath containing 10 ml. of the above solution. The bath after sorption was titrated against $\frac{N}{100}$ sodium hydroxide as in the last experiment . The constant titre value in each case was somewhat lower than the titre value for the blank reading. This indicated that a chemical reaction was taking place between the acid and the film. This was not unlikely, since the sulphonic acids are strong acids and would dissolve a part of the film.

This also indicated that the proton of the sulphonic group is probably not acting as an acceptor to form a hydrogen bond. Hydrogen-bond formation by hydrogen of a sulphonic acid molecule is not reported anywhere in the literature and it is not known whether it ever forms such a bond. Benzene sulphonic acids though strong however, may not be completely ionised and some unionised molecules could form hydrogen bonds. Why this does not happen is not known. Miss McCarter (143), working in these laboratories, has recently obtained evidence, however, which suggests that the unionised molecules of benzene sulphonic acid may be able to form a bond with ketonic groups in fibrous surfaces.

D. Miscellaneous.

We will describe in the following pages the results of experiments which were performed to test the validity of some of the conclusions arrived at by earlier work. They do not form a homogeneous set which can be included under one heading. Although the experiments were carried out with great care, they are not meant to be quantitative in nature and hence should be regarded as qualitative. In each case, however, duplicate sets of readings were taken to test the reproducibility of results.

1. Sorption of Catechol, Resorcinol and Hydfoquinone.

The aqueous solutions of catechol, resorcinol and hydroquinone were prepared by dissolving 1.0 gm. of pure product (supplied by Messrs. British Drug Houses Ltd.) in 500 ml. of distilled water. The sorption baths in each case were prepared by diluting 5 ml. of the solution to 50 ml. with water and the sorption was carried out for 24 hours at 40°C. The baths left after sorption were estimated by titration, by the potassium permanganate method described in detail in the earlier section (p.71). This method was also used for the estimation of hydroquinone. (In Part II Section II mention is made of resorcinol and catechol only.)

Approximately 0.1 N potassium permanganate was standardised by titration with 0.1 N sodium oxalate in presence of sulphuric acid. The normality of the permanganate was found to be 0.09804

The normality of the sodium thiosulphate solution was determined by titration with potassium permanganate and it was found to be 0.9922 . The following Table contains the sorptions of three compounds.

Table 32.

Sorptions of Catechol, Resorcinol and Hydroquinone at 40°C

Initial concn. - 0.091 millimole per litre.

	Amount sorbed in millimoles/Kgm. film. (DUPLICATE READINGS)			
Catechol	(i)	298.1	(ii)	295.6
Resorcinol	(i)	48.2	(ii)	49.9
Hydroquinone	(i)	230.5	(ii)	233.7

The anodised foils dyed with catechol had a deep, dirty green colour. This may indicate that catechol forms a co-ordinate complex with the metal. Catechol is also known to oxidise to a deep green product and perhaps the colour of the foil may be partly due to the sorption of the oxidised compound by the film.

It will be noted that resorcinol was much less sorbed than hydroquinone. This may probably be due to the fact that resorcinol is known to be associated by the formation of strong intramolecular hydrogen bonds (144) and does not have a free hydrogen to form a bond with the film. The small sorption,

however, may be due to the presence of some unassociated resorcinol molecules in the solution. Hydroquinone is sorbed in an amount comparable with that of catechol. The purpose and usefulness of these experiments will be indicated later.

2. Sorption of Donor Compounds.

If we accept the mechanism of hydrogen bond formation as due to a proton acting as acceptor of electrons one of the two anions which are bonded can be called a donor. For the sake of simplicity, we shall call compounds which do not contain a bond-forming hydrogen atom, but contains a donor anion "donor compounds". It will have been realised that so far we have assumed that the aluminium oxide of the anodic film is a donor compound. As we have discussed in the introduction, even though nothing definite is known about the film structure, it could be safely assumed from all the available evidence that the film consists of γ-alumina. It is evident that if the film is dried carefully, there is no likelihood of there being a hydrogen atom in the film molecule to take part in bond formation. The only other possibility is that the film might be a monohydrate of alumina. It has been pointed out by Bernal and Megaw (155) that diaspore, (ß-monohydrate) and böhmite (α-monohydrate), the two known monohydrates of alumina, have the same structure, as indicated by X-ray powder photographs. Ewing (112) has shown that diaspore has a hydrogen bond within the molecule. Thus, even if the film was an alumina monohydrate, there would not be a free hydrogen in the

molecule to act as an acceptor. Thus it will be evident that it was not unreasonable on our part to assume that the aluminium oxide of the film is a donor compound. It should be pointed out here that even if the mechanism of hydrogen-bond formation was not of the donating-accepting conception as assumed but of electrostatic attraction between the atoms concerned in the bond formation the arguments outlined above are equally applicable.

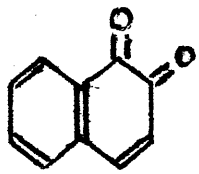
If, as we suggested, alumina is only a donor compound and sorbs compounds which form hydrogen bonds, other donor compounds would not be sorbed from non-aqueous solutions. Six known donor compounds, therefore, were selected and experiments to sorb each on the film were carried out. First of all each compound, and the experimental conditions will be described. All the experiments were made in "Quickfit" test tubes. At least two readings were taken in each case.

(i) Nitrobenzene:-

Pure nitrobenzene was distilled twice, to obtain a faintly coloured liquid. After discarding the first few ml. of distilled liquid, 0.940 gm. of the clear nitrobenzene was dissolved in 200 ml. of dry Analar benzene. Sorption tests on the film were made from baths containing 25 ml. of this solution, for 48 hours at 40°C. Two readings were taken. The concentration in the baths after sorption was estimated on the absorptiometer, using ultraviolet light, and compared with a blank run for the same time without foil. It was found that the nitrobenzene is

not sorbed at all under these conditions.

(ii) ß-Naphthoquinone:-



The solution was prepared by dissolving 0.125 gm. of the pure substance in 500 ml. of dry benzene. Sorption tests were made from 25 ml. baths containing 10 ml. of the above solution, for 48 hours at 40°C. As in the previous case, the concentration of the baths left after sorption was determined on the absorptiometer, using ultraviolet light. Comparison with the blank showed that no sorption had taken place.

(iii) ß-Naphthylamine:-

The solution of 0.125 gm. of pure compound in 125 ml. of dry benzene was used. The sorption tests in triplicate, were made from 25 ml. of the solution, for 48 hours at 40°C, and again it was found that the compound was not sorbed. The estimation was made as before on the absorptiometer, using ultraviolet light.

(iv) Anthraquinone:-

The commercial product was purified by sublimation to give long yellow needles. The solution was prepared by dissolving

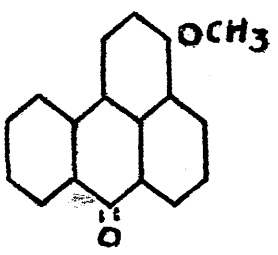
0.125 gm. of this purified substance in 125 ml. of dry benzene. The baths for sorption were made up by diluting 20 ml. of this solution to 25 ml. with dry benzene. Sorption tests on the film were made by keeping the foil in the bath for 48 hours at 40°C. The absorptiometer, with ultraviolet light, was used to determine the concentration of the baths after the tests. Again, it was found that no sorption took place.

(v) ß-Aminoanthraquinone:-

The solution was prepared by dissolving 0.02 gm. of pure compound in 200 ml. dry benzene. This compound was found to be very sparingly soluble in benzene. Sorption tests were made from 25 ml. of this solution, for 48 hours at 40°C. The baths left after the tests were estimated on the absorptiometer using ordinary light and the Blue (No.602) Ilford light filters. On comparison with a blank, it was found that no sorption had taken place.

(vi) Duranol Brilliant Yellow 6G (I.C.I.):-

The dye has the following constitution



The commercial sample of the dye was purified by crystallising from the mixture of alcohol and water. The pure product was very carefully dried and its solution in dry benzene prepared by dissolving 0.135 gm. of the dye in 250 ml. The sorption baths were made up by diluting 10 ml. of this solution to 25 ml. with dry benzene. The sorption was tried for 48 hours at 40°C. The baths left after sorption were examined as in the case of ß-aminoanthraquinone and it was found that the dye was not sorbed at all.

Duranol Brilliant Yellow 6G and ß-aminoanthraquinone had deeply coloured solutions and if the sorptions had taken place, the anodic film also would have been visibly coloured. This was not observed and it provided an additional check. It should be mentioned here that these sorption experiments were made on very carefully dried anodic film. The absence of sorption in the case of all the compounds described above seem to justify our assumption that the alumina of the film does not contain a hydrogen atom which can form a bond by joining the anions. It also showed that even though the hydrogen atom of the amino group is known to take part in the formation of a hydrogen bond, it does not do so in the present case, probably because of the basic character of the group. The methoxy group in the dye Duranol Brilliant Yellow 6G also does not take part in hydrogen-bond formation from non-aqueous medium.

It was stated earlier that the reason why some compounds not having a free hydrogen were sorbed from aqueous solutions

was that a water molecule formed a bridge between the anions of the sorbed compound and the film. If this were possible, dihydroxy compounds like hydroquinone may also be able to act as a bridge, provided steric hindrance does not prevent it from doing so. In the preceding experiment, the sorption of catechol, resorcinol and hydroquinone on the film was studied. It was seen that catechol forms a co-ordinate complex, while resorcinol is not well sorbed. It was thought, therefore, that hydroquinone would be the best for this experiment. Three donor compounds were selected from the six just described. These compounds had fairly deep coloured solutions and were expected to give a coloured film if they were sorbed. Two sets of experiments were performed in each case - one containing hydroquinone and the other containing dry phenol. It will be expected that no sorption will take place from solutions containing phenol. Both the hydroquinone and the phenol solutions contained 0.50 gm. pure dry substance in a litre of dry benzene. The sorption baths were made up of 10 ml. of solution of donor compound, 10 ml. of phenol or hydroquinous solution and 5 ml. dry benzene. The experiments were continued for 48 hours at 40°C. The following Table contains the results:-

Table 33.

Sorption of donor compounds in benzene solutions in presence of hydraquinone and phenol.

Contents of sorption bath.	Amount sorbed (Moles/Kgm).
Naphthoquinone + phenol	Nil
" + hydroquinone	38.8
ß-aminoanthraquinone + phenol	Nil
" + hydroquinone	43.3
Duranol Br. Yellow 6 G + phenol	Nil
" + hydroquinone	38.4

The results show that hydroquinone acts as a bridge in all the three cases and consequently the donor compound is sorbed. We are conscious of the fact that the amounts sorbed are very small, but the additional check was provided by the coloured film surfaces obtained in each case where the compound was sorbed. This supports the suggestion made earlier that water and dihydroxy compounds like hydroquinone can act as bridges and that sorption on the film would result from the solution of a donor compound in presence of such a bridging compound.

3. Qualitative Experiments:-

Some of the following experiments were made qualitatively in order to examine the effect of certain groups in a molecule on its sorption on the film. Some of them were confirmatory tests only.

(i) Aniline:-

This was dissolved in dry benzene and the solution used for sorption on anodic film. The anodised strip was allowed to remain in approximately 50 ml. of a 1% solution of aniline for 24 hours at 40°C. The foil after allowing to dry in air was transferred to a beaker containing sodium nitrite. Soon after the foil was placed in the beaker, a few drops of hydrochloric acid were added. After keeping the foil for about ten minutes, it was taken out and placed first in sodium acetate solution and then in another beaker containing a solution of ß-naphthol in alkali. No colour was observed to be developing. This showed that aniline is not sorbed. We also found, as mentioned in the preceding section, that ß-naphthylamine is also not sorbed.

To confirm that diazotisation on the film could be done, Princuline O was sorbed on the film and the diazotisation carried on as detailed above. A bright red colour developed on the film as soon as the foil was placed in ß-naphthol solution. This showed that if the compound is sorbed on the film, it will still diazotise and couple.

(ii) p-Anisidine:-

This was used under the same conditions as aniline and the aluminium strip was treated with sodium nitrite and hydrochloric acid for diazotisation as mentioned above. No colour developed in this case, again showing that the substance is not sorbed.

(iii) m- and p-Nitroaniline:-

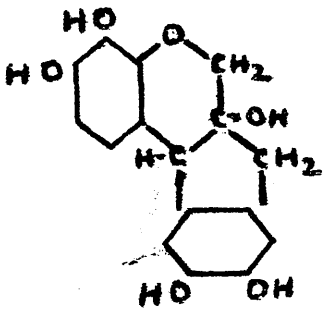
Similar sorption trials were done with these substances but the results in each case were entirely negative.

These qualitative experiments indicate that amino and methoxy groups do not form a hydrogen bond with the film. The C - H link in the methoxy group is not sufficiently electronegative to permit it to attract sufficiently an adjacent negative atom. Hydrogen bonds formed with hydrogen attached to carbon are not known. Hydrogen-bond formation by the hydrogen of the amino group is, however, reported quite often. It is difficult to say why an amine is not attached to the film by such a bond. The basic character of the group may probably have something to do with it.

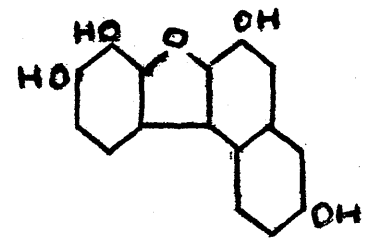
(iv) Haematoxylin and haematoxylone:-

Haematoxylin (I), the colouring principle of the natural product, logwood, is used to produce black shades on wool. "Haematoxylone" was synthesised and named so by Duff (145). According to him it has the

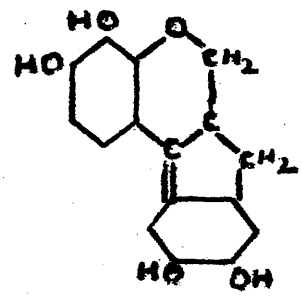
following structure (II) :-



Haematoxylin (I)



Haematoxylone (II)



Haematein (III)

The anodic film was dyed a deep violet shade from the solutions of both these compounds. Haematoxylin, which readily oxidises to the o-hydroxyketone, haematein (III), in air, probably does so in the treating bath. Haematein is known to form co-ordinate complexes with metal atoms, and the colour of the dyed film in this case was also perhaps due to the metal complex formation. The purpose of the experiment was to see whether such a

natural colouring matter and an analogous synthetic compound would dye the film or not and if they did so whether the shade could be added to a range of useful dyes for anodised aluminium. It was found that the shade given by these products is of an unattractive tone, but before anything definite could be stated about its practical application many other factors, including the fastness to light and water would need to be determined.

(v) Neolan Blue B (I.C.I.) and Carbolan Crimson B (S.C.I.)

These two dyes were also tried. Both of them gave fine level shades of attractive brilliance, which had very good washing fastness. The Neolan dye is a co-ordinate complex with a chromium atom in the molecule. This dye, therefore, may be forming a double metal complex with the anodic film similar to the Turkey-red complex, the structure of which has been indicated in the introduction. It is to be expected that such double complexes will have good fastness properties like Turkey-red itself. The Carbolan dye is an ordinary azo acid dye with a long alkyl chain (C_{12}) attached. This evidently does not prevent its entry into the pores of the film. It appears that the structures of these dyes make them very suitable for use in dyeing of anodised aluminium, and hence their application in commercial practice.

4. Action of water:-

We have very often referred to the action of hot water,

which results in the "sealing" of the film. As indicated in the introduction this sealing is done in many ways, but boiling in water or st/eaming the anodised foil are the treatments usually given. It appears that this process of sealing brings about a chemical change in the structure of the film. It has been shown by many workers that the γ-alumina of the film is converted to a monohydrate consisting of larger crystals, by such treatments, thus reducing the porous nature of the film. Pullen (31) by chemical analysis of sealed films found that the water content was equivalent to two molecules per molecule of aluminium oxide. As a dihydrate of alumina is not known, he suggested that the sealed film consists of a monohydrate with a molecule of water held in the lattice. Similar instances of two types of sorbed water are reported very frequently in the literature. Many crystalline compounds are hydrates, the water molecules being held by a covalent link. Sidgwick (126) pointed out that water can take part in bond-formation either by donation of electrons on the part of oxygen or by acceptance on the part of hydrogens. The water molecules bound in this way will be firmly held, but there are crystalline compounds in which the degree of hydration is more than can be accounted for by the maximum covalency of the atom to which the water molecules are co-ordinated. The X-ray examination of these substances reveals that, while some of the water molecules are attached by co-ordinate covalencies, others are distributed in convenient spaces in the crystal lattice. There they may

be held by van der Waals forces or they may form weak hydrogen bonds with other atoms in the lattice. It seems that they owe their place to the geometry of the lattice. This type of water is often easily lost (146). Astbury (147A) has observed that the water that proteins can take up appears to be broadly of two kinds; the "loosely bound" and the "tightly bound" ("or rather the less loosely bound, since there is probably no hard and fast distinction"). These views are in accordance with Pullen's suggestion of the existence of two types of water in the anodic films after boiling in water. The tightly bound water molecules may be held by covalencies or hydrogen bonds; and thus when such a film is put in a dye solution no dye will be sorbed probably because no anions which could donate electrons are available, in other words, no free sites for sorption of dye exist. The lattice space will also be occupied by loosely-held water molecules, and hence dye molecules possibly cannot be accommodated even there. It was observed that if a sealed anodised aluminium foil is heated strongly and cooled in a desiccator, it then sorbs dye to some extent. This sorbed dye, however, appears to be loosely held, since it can be easily removed by treating the dyed foil with a suitable solvent, e.g. pyridine. It will be recalled that freshly anodised and dyed piece could not be stripped completely of its dye content by treatment with any organic solvent. This can be explained by assuming that the loosely-bound or lattice water in the anodic film is removed by the heat treatment. The dye

molecules can now occupy the vacant spaces in the lattice, but evidently they will not be held by strong forces and hence they can be leached out by treatment of the foil with suitable organic solvents. It is known that the alumina monohydrate is very stable and heating up to temperatures of about 300°C does not materially alter this hydrate. This suggests that the tightly bound water will probably be linked covalently and not by hydrogen bonds, because it may be expected that hydrogen bonds would be ruptured by treatment of the foil at high temperature. The alumina thus would regain its dye sorption activity.

(5) Zeta-potential of the anodic film:-

Throughout the discussion in the preceding pages, we have assumed that the anodic film bears a positive charge. We will now attempt to show that the assumption is justified.

It is known that sols of metallic hydroxides and hydrated oxides carry a positive charge. Harrison (147), by electrophoresis measurement, demonstrated that aluminium oxide in water possessed a positive charge. We, therefore, supposed that the film, which consists of aluminium oxide only, will bear a positive charge. This was supported by the observation that basic dyes, the colour ions of which carry a positive charge, are not sorbed by the film, unless it is mordanted with the usual mordants for such dyes, e.g. tannic acid.

Aluminium anodised in the usual way, was mordanted with 200 ml. of tannic acid solution (5 gm. per litre) at 80°C for half an hour, then washed with cold water. Four pieces (2" x 1") of the treated film were then dyed at the same temperature with a 0.1 gm. per litre solution of Magenta PS in water (Colour Index No. 677) for different durations. The amounts of residual dye in the bath were estimated on the absorptiometer. The following Table contains the results.

Table 34.

Sorption of Magenta PS on mordanted anodic film at 80°C.

Amount of standard dye sorbed at 80°C (millimoles/Kgm.)			
15 mins.	60 mins.	120 mins.	240 mins.
261.6	263.2	262.3	262.3

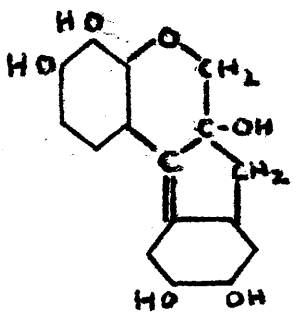
It will be noted from the Table that whatever dye is sorbed by the mordanted film is sorbed immediately. This indicates that the dye is taken up by the mordant only. Since the reaction between dye and mordant is a stoichiometric one, the dye taken up will be a constant amount relative to the mordant. It has been observed, however, that the dye on the foil dyed in this way is not very fast, and can be removed by organic solvents.

This is perhaps because the film has no very great affinity for tannic acid and the bond between the dye and the film will not be very strong. It was also observed that basic dyes are taken up if the film is stained with grease. It will be evident that in this case, too, the grease acts as a "mordant", but it will only be on the surface and both the grease and the dye can be removed by treatment with organic solvents, e.g. carbon tetrachloride, which dissolve away the grease.

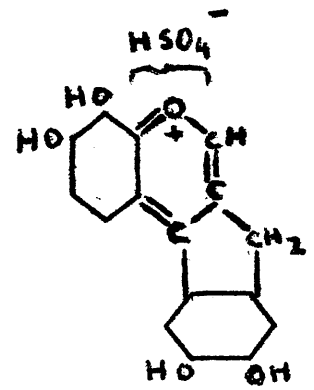
From the point of view of electrostatic forces, the dyeing of anodic film with basic dyes can be compared with the dyeing of cellulosic fibres with direct dyes. The effect of addition of salt to such a dyebath has been investigated by Neale (58). He has reported the measurement of surface potentials of undyed fibres such as bleached cotton, nylon, silk, scoured wool, in sodium chloride solutions, which show that in all the cases the charge on the surface decreases as the concentration of salt in solution increases. The direct dyes with high basicity like Chlorazol Sky Blue FF are not sorbed from solutions in the pure state, due to repulsion between the dye anion and the fibre surface; but on reducing the surface potential by adding common salt to the bath, they do dye the fibre. It was thought that sodium chloride might have a similar action in reducing the positive potential of the film surface and then perhaps the basic dyes would be taken up. Two basic dyes - Chrysoidine Y (Colour Index No.20) and Bismarck Brown G (Colour Index No.331) were selected. Anodised

aluminium strips were left in dyebaths containing 5% solutions of these dyes with and without 5% and 10% of sodium chloride respectively, for 16 hours at 40°C. It was found at the end of the period that the dye from the baths containing sodium chloride had dyed the film while the anodised aluminium strips in the blank dyebaths was not dyed at all.

The dyeing of the anodic film with haematein and acid iso-haematein sulphate, two compounds prepared from Logwood extract, confirmed the above hypothesis. These two substances (kindly supplied by D.J.Duff), have the following constitution:-



Haematein



Acid iso-haematein sulphate

It is evident from the above that in acid iso-haematein sulphate the haematein part of the molecule forms a cation. It will, therefore, not dye the anodic film. The dye trials with both of these showed that haematein does dye (a deep purple shade) on the film, and the iso-haematein sulphate merely stained it a weak shade.

Conclusive evidence of the positive potential of the film surface has been given by Johnston (148). By electrophoresis measurements in a U-tube containing a suspension of the ground anodic film prepared by anodising the foil right through and dissolving away small remaining portions of metal in hydrochloric acid, before grinding in a mortar and pestle, he found that the film had a positive surface charge which could be neutralised by 0.70 per cent. sodium chloride. (Before the test the ground film was repeatedly washed with distilled water until free of acid.) It should, however, be noted that the surface potential so acquired is with respect to the dispersion medium. It will be expected that the film will have no charge in benzene, for Jensen and Gortner (149) found that the zeta-potential of benzene and carbon tetrachloride-aluminium oxide interface was zero.

In the above treatment, the effect of the surface is considered as it affects the sorption of dyes of different types. Since microscopic observation shows that the dye is not confined to the mere external surface, we can assume that the surface effects will involve both the external and the internal surface. Neale (58) suggests that the internal surface of a textile fibre, with pores long compared with their width, can be regarded as equipotential. The anodic film, it has been observed, has also long narrow pores, and if we regard the internal surface as equipotential, the dye molecules approaching the film surface will be affected by the potential on the external

surface. The basicity of the dye molecule will play a part here, but as soon as the dye is adsorbed on the external surface, the internal surface will offer the same conditions for its passage or diffusion inside, no matter what its initial charge may have been, provided other factors such as structure of the dye molecule or its particle size do not interfere. Thus, if dye molecules with different charges (e.g. with different numbers of sulphonic groups per molecule), but with otherwise almost the same configuration were taken and their sorption studied, the dye with the greater charge should have the greater difficulty in diffusing inside, because of the attraction between the molecule and the external surface. Once the effect of this attraction is overcome, diffusion inside the film will proceed steadily because as we have assumed, the film has an equipotential internal surface and part of the charge of this equipotential surface will have been neutralised by the sorption of oppositely charged dye ions. Sneddon (133) observed that the diffusion curves of Naphthalene Red JS (Colour Index No.176) , Naphthalene Red EAS (Colour Index No.182) and Naphthalene Scarlet 4RS (Colour Index No.185) containing one, two and three sulphonic groups respectively, but the same basic structure, behave in this way. The curves showing amount of dye on foil, vs the square root of the time show that after overcoming the initial obstruction, each dye has an identical rate of diffusion inwards, since the curves are parallel straight lines. Before this stage is reached the dyes face increasing difficulty in overcoming the

attraction of the external surface, as the charge on their ions increases.

These observations, therefore, indicate that the charge on the surface of the film plays a very important rôle in dyeing. We have postulated that the initial attraction of the dye anion for the film is the effect of the play of long-range electrostatic forces, due to this electrical potential difference. Once the dye anion is brought nearer the surface by such forces, many other forces, usually called short range forces, operate and the passage of the ions inside the complicated film structure and final attachment to the sites in the film are dependent on them.

General Discussion.

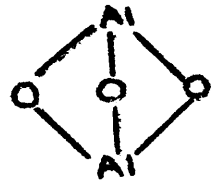
We have seen in the preceding pages that molecules of acid dyes appear to be attached to the anodic film through hydrogen bonds. It was pointed out during the review of existing knowledge on the conditions for the formation of strong hydrogen bonds that it is very difficult to produce positive evidence to prove the formation of such bonds when substances like the dyes and the anodic film are involved.

The mechanism of hydrogen bond formation has given rise to considerable speculation. It occurs only when the anion which is bonded possesses a lone pair of electrons and can act as what may be called a donor. The question then is whether the hydrogen atom can be regarded as an acceptor. Hydrogen contains only one shell, which cannot possible contain more than two electrons without the breach of the Pauli exclusion principle. Two suggestions have been put forward to account for the hydrogen bond. The first is based on resonance. It is assumed that resonance occurs between the two forms A·····H - B and A - H·····B and the actual state would be represented by a hybrid of the two. This hypothesis accounts for the necessity for A to have a lone pair which it is prepared to donate and for B to hold the lone pair when the proton is linked with A i.e. both the atoms should be sufficiently negative in character. The second suggestion is that the hydrogen bond is mainly electrostatic in nature. If A is negatively charged and H - B is a strong dipole, then

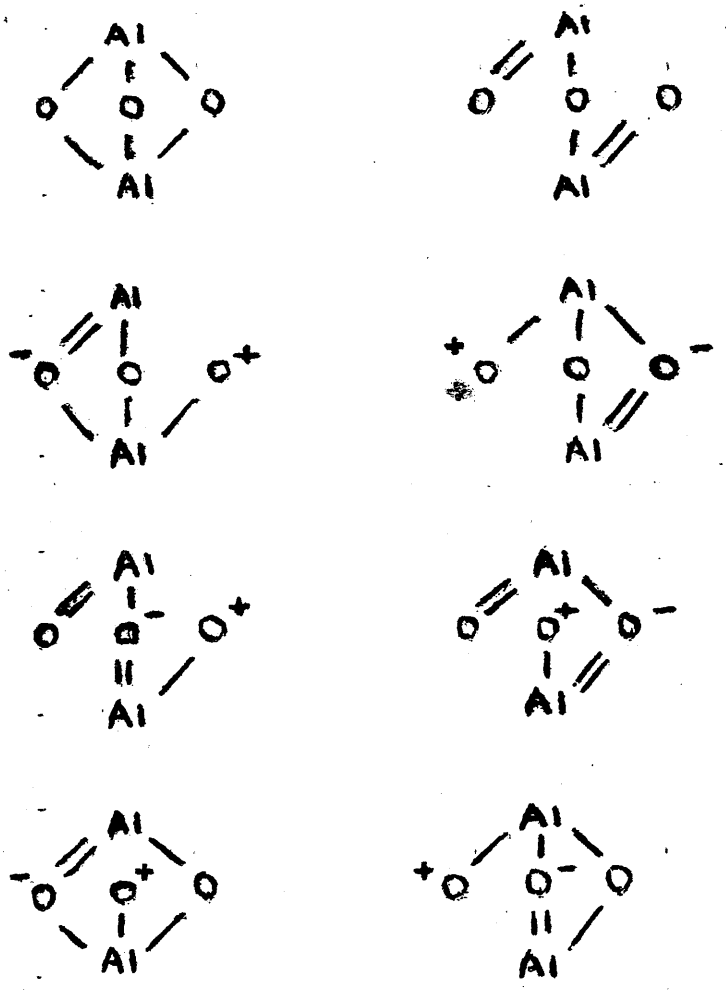
A.....H - B may give a strong link. Martin (150) suggests that in the liquid state and for simple molecules, dipole interaction and hydrogen bonding are equivalent ways of describing the same thing. Both these mechanisms may be partly responsible for the formation of the hydrogen bond. It will be noted that both conceptions necessitate the existence of negative atoms which may be bonded by hydrogen and that the more negative they are, the stronger the nature of the bond. Resonance within the structures of molecules that are bonded tends to make the anions more negative, as in the case of carboxylic acid dimers, and to make hydrogen more positive, as in the phenols.

Now we will apply this conception to the present case. The types of hydrogen bonds involved here are O·····H - O and N·····H - O . Bonds of this type are well known. The oxygen atom and the nitrogen atom concerned in each type have a lone pair of electrons, which they can donate. We should now see whether there is any possibility of resonating structures, which as mentioned above will tend to make the oxygen atom of aluminium oxide more negative.

The ordinary valence-bond structure of aluminium oxide may possibly be represented as



This is a completely covalent structure. According to Pauling (108,p.70) bonds between oxygen and any of the metals are 50 per cent, or more, ionic. The electronegativity difference of the atoms, aluminium and oxygen, is 2.0 which suggests that the aluminium-oxygen bond has 63 per cent. ionic character (loc.cit.) The aluminium oxide molecule may therefore be described as resonating among the following canonical structures:-



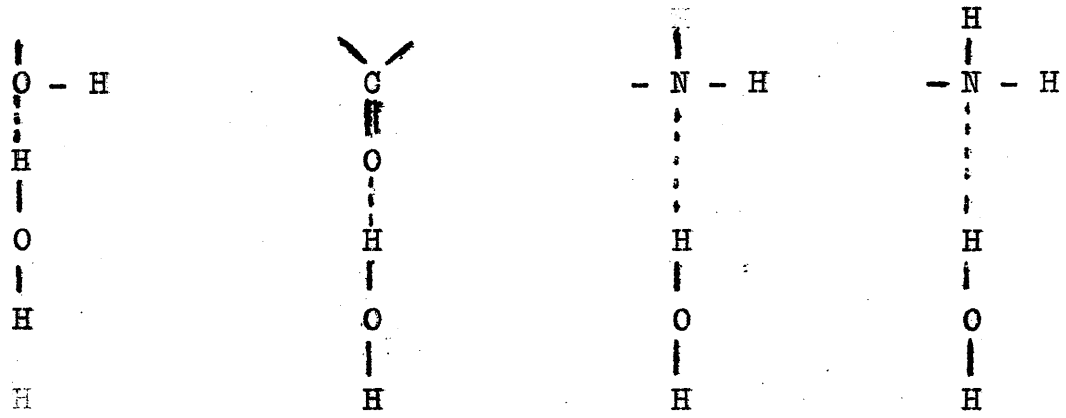
and so on. The ionic structures constitute 63 per cent. and the covalent structures 37 per cent. of the normal state of the molecule. The tetrahedral covalent radius of the aluminium

atom is 1.26 Å and the single-bond and double-bond covalent radii of the oxygen atom are 0.66 Å and 0.55 Å respectively. The cation-oxygen distance in the aluminium oxide molecule having a 100 per cent. covalent structure will therefore be 1.92 Å. It is not known what proportion out of 67 per cent. each canonical structure contributes to the ionic character. If we assume that all of them are in equal proportions, the cation-oxygen distance in a stable molecule will be 1.89Å which agrees exactly with one of the two values given by Megaw (151).

It will be seen thus that resonance among the various structures of aluminium oxide increases the electronegativity of its oxygen atoms and consequently the possibility of hydrogen bond formation. The primary condition for the formation of the bond, of course, will be that the potentially bonding groups should come sufficiently closer to enable the attraction forces to come into play. In the case of molecular bonds like the present one, it is normally not difficult to achieve this, provided the interacting groups are situated prominently on some outer portions of the molecule. It will not be too unreasonable to assume that it is so in the case of dyes and the aluminium oxide we have been considering.

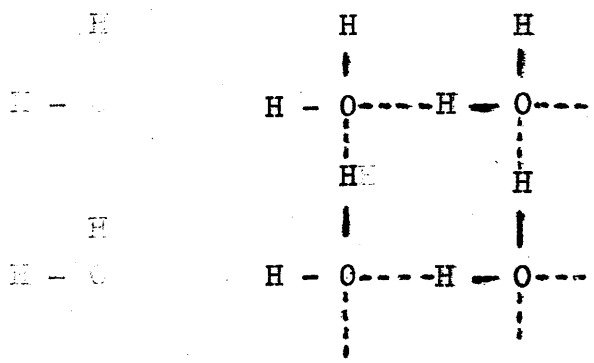
In the case of Orange II and Azo Geranine 2G we have suggested that the dye is attached to the film by a bridge formed by water molecules, thus forming two hydrogen bonds. By studying the absorption of water by proteins, Jordan Lloyd and her collaborators (153) have suggested that the tightly bound

water is linked by hydrogen bonds with the oxygen and nitrogen atoms of the carbonyl, hydroxyl, imino and amino groups of the protein structure and can be represented thus



hydroxyl carbonyl imino amino

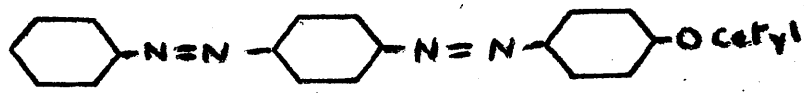
This shows that one hydrogen atom of the water molecule forms a bond with a nitrogen atom or oxygen atom. That both the hydrogen atoms can simultaneously form bonds with different anions is well known (e.g. 163 and 164) and can best be illustrated by the structure of water itself:-



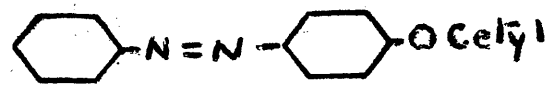
The possibility of one or both nitrogen atoms of an azo group taking part in the hydrogen bond formation has been clearly demonstrated by Rose (152). He has measured the dielectric

constants of azobenzene-phenol mixtures in various proportions and has found that the curve obtained by plotting percentages of the two components against the dielectric constant values shows a decided break when the molecular proportions of phenol and azobenzene are 1:1 . The curve also shows a much less distinct break when the proportions are 2:1 . This suggests that the second nitrogen atom of the azo group does not easily form a bond. This is perhaps why we found that benzeneazo-ß-naphthol, in which one nitrogen atom is already involved in a hydrogen bond with the adjacent ortho-hydroxy group, could not form another bond, and consequently was not sorbed from aqueous alcoholic solution. The presence of an ionised sulphonic group with electron-repulsive properties in the benzene nucleus of Orange II and Azo Geranine 2G may make the nitrogen atom of the azo group not involved in the hydrogen bond more electro-negative and thus increase its hydrogen bonding power, resulting in the mechanism of sorption we have suggested. Rose (loc.cit.) has also shown that acetanilide does not form strong hydrogen bonds with azobenzene, phenol, aniline or triethylamine. This suggests that the $-NHCOCH_3$ group in Azo Geranine 2G is not taking part in hydrogen bond formation. Thus we are left with the possibility of two hydrogen bonds between the dye molecule and the film (through a water molecule), which agrees with the values of heats of reaction obtained in each case. Neustadter (154) has found that a compound having

the structure:-



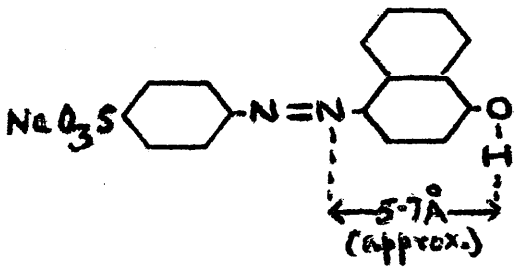
forms a monomolecular film on water whereas the compound:-



does not form a monomolecular film. This, then, shows that the azo group has a slight but definite attraction for water. In other experiments, he has shown that this attraction is much less than that of the phenolic hydroxy group.

It is not important to know whether the second point of attachment in the case of Orange I is to an oxygen atom of the same aluminium oxide molecule as the first, or to some other oxygen atom, because there will in any case be a far greater number of aluminium oxide molecules than of sorbed dye molecules. It is, however, unlikely that the two points of attachment of one dye molecule will be on the same aluminium oxide molecule, because the distance between the oxygen atoms in aluminium oxide on the one hand and between the nitrogen and oxygen atoms in Orange I are not comparable. We

have seen that the cation-oxygen distance in aluminium oxide is 1.89 Å, while the cation radius as given by Zacharisen [quoted by Bernal and Megaw (155)] is 0.55 Å. The effective oxygen radius in the aluminium oxide molecule is, therefore, 1.34 Å and the -O - O- distance 2.68 Å. The distance between the nitrogen and oxygen atoms in Orange I :-

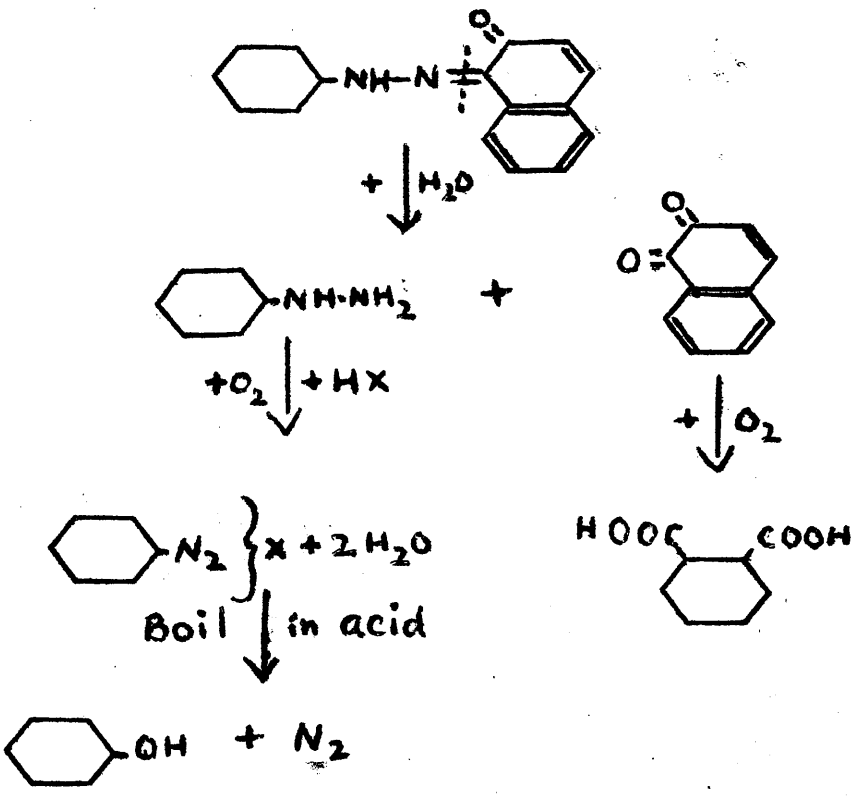


is approximately 5.7 Å (assuming the hydroxyazo structure of the dye).

The value of heat of reaction obtained from the isotherms of benzeneazo- ∝ -naphthol shows that the energy of the O·····H - O bond between the anodic film and the dye is of the order of 4.0 K.cal. This confirms the possibility of three hydrogen bonds in the case of Orange I (12.0 K.cal.) and two in the case of Orange II (8.0 K.cal.)

Assuming that the mode of attachment, as outlined in the preceding pages, is through hydrogen bonds, it should be interesting to study the fastness of dyed anodised aluminium. We have mentioned the results of desorption of dyed pieces (p.141). Even though it is difficult to base definite conclusions on the results of three dyes only, it appears from the

study of mechanism of sorption that dyes with a hydroxy group in the para-position to the azo linkage will probably have greater fastness to hot water than those having a hydroxy group in the ortho-position. The other important fastness property so far as dyed anodised aluminium is concerned will be light fastness. It is to be noted that this property will not so much depend upon the bond of attachment of the dye molecule to the film as will the washing fastness. The mechanism of light fading is not yet understood. Desai and Giles (156) attempted to explain the fading of azo dyes by an hypothesis involving oxidation. They suggested that the dye in the form of the hydrazone tautomer is hydrolysed, and the products are then further oxidised. The series of reactions was illustrated as follows:-



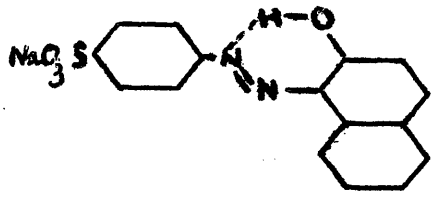
They assumed that the light fading of azo dyes is due to a similar sequence of reactions. It will then be obvious that those dyes which exist preponderantly in the azo form should be faster to light than those in the hydrazone form. They found that some light fading results, particularly of insoluble dyes, agreed with the above hypothesis, while water soluble dyes gave contradictory results. Desai (157) studied the fastness of anodised aluminium dyed with a series of azo dyes and obtained interesting results which are summarised in Table 35 given below. The R-acid (ß-naphthol-3:6-disulphonic acid) series of dyes have the hydroxy group in the ortho-position to the azo group and the oxy-L-acid (∝-naphthol-6-sulphonic acid) series have it in the para-position. The fastness numbers were determined by the official B.S.I. standards as originally established by the Society of Dyers and Colourists, Fastness Tests committee; the lowest fastness being Grade I and the highest, Grade 8 on this scale.

Table 35.

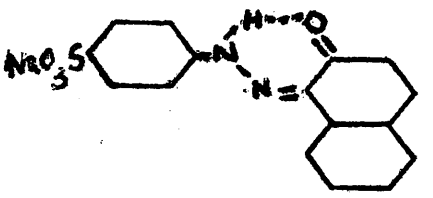
Light fastness of Soluble Azo Dyes on Anodised Aluminium.

Dye	Light fastness	Dye	Light fastness
Orange II	2	Aniline → oxy-L-acid	3
Orange I	1	o-nitroaniline → "	3
O-methyl ether of Orange I	4	m-nitroaniline → "	2
Aniline → R-acid	2	p-nitroaniline → "	1
o-nitroaniline → "	2	o-chloroaniline → "	1
m-nitroaniline → "	2	m-chloroaniline → "	1
p-nitroaniline → "	2	p-chloroaniline → "	1
o-chloroaniline → "	1	2:4 dichloroaniline → "	1-2
m-chloroaniline → "	2	m-toluidine → "	1
p-chloroaniline → "	1	p-toluidine → "	3
2:4 dichloroaniline → "	1	o-anisidine → "	1
m-toluidine → "	2	p-anisidine → "	2
p-toluidine → "	1	Metanilic acid → "	1
o-anisidine → "	2	Sulphanilic acid → "	1
p-anisidine → "	1	Anthranilic acid → "	2
R-acid ← Dianisidine → R-acid	1	p-aminobenzoic acid → "	1
Metanilic acid → "	3		
Sulphanilic acid → "	1-2		
Anthranilic acid → "	3		
p-aminobenzoic acid → "	4		

Of the two resonating forms of Orange II :-



azo form



hydrazone form

the hydrazone form containing the $-N = C<$ bond is more likely to form a strong hydrogen bond with a water molecule than the azo form having $=N - C\leqslant$ because of the greater electronegativity difference and ionic character of the former link. If that is true, Orange II on anodised aluminium will be faster to washing when it is in the hydrazone form than when it is in the azo form while according to the Desai-Giles hypothesis the contrary will apply to the light fastness. Thus high fastness properties in both respects will be incompatible.

The effect of the position of substituents in increasing the light fastness is quite interesting. This is summarised in Table 36. It will be generally observed that the presence of a carboxyl or sulphonic group in the benzene ring increases the fastness though the effect is more marked in the case of R-acid dyes than in the case of oxy-L-acid dyes.

Table 36.

Effect of substituent groups in R-acid and Oxy-L-acid dyes, shown in decreasing order of light fastness.

R-acid	Oxy-L-acid
p - COOH	o - NO_2
o - COOH	p - CH_3
m - SO_3H	m - NO_2
o - NO_2	p - OCH_3
m - NO_2	o - COOH
p - NO_2	2:4-Cl_2
m - Cl	p - NO_2
m - CH_3	o - Cl
o - OCH_3	m - Cl
p - SO_3H	p - Cl
o - Cl	m - CH_3
p - Cl	o - OCH_3
2:4-Cl_2	m - SO_3H
p - CH_3	p - SO_3H
p - OCH_3	p - COOH

A glance at Table 36 indicates that the effect of the groups is roughly in the reverse order in the two series of dyes,

which might suggest that the factors operating in light fading are of an opposite nature in the two sets of dyes. Nothing definite can be said about these factors until the mechanism of light fading is more clearly understood.

The discussion of the experimental observations outlined so far has shown that the problem of sorption of dyes by the anodic film is more complex than it may at first appear. It will be extremely difficult to put forward one compact hypothesis because there are many processes involved. There may be many facts which could not be explained by our present knowledge. Desai (157) observed that the dyes, sulphanilic acid → phenol, naphthionic acid → phenol and their O-methyl ethers were not sorbed by the anodic film. Chipalkatti, using an apparatus designed on the basis of the McBain-Bakr spring balance (158) studied the sorption of water vapour on anodic films from aluminium anodised right through and found that the amount taken up was negligible (142). We are not able to explain these observations at this stage. Perhaps more detailed investigation may clear up these and many other problems which may arise later and are difficult of solution by the present hypothesis.

SECTION III.

Practical Aspects of the Work.

It is intended to discuss here in brief the practical contribution of this work towards understanding the process of dyeing anodised aluminium.

Quantitative sorption tests on mordant dyes have proved that the combination between the dye and the anodic film is chemical and hence dyes of that class in general are likely to be faster than ordinary acid azo dyes. Among the acid dyes those with hydroxy group para- to the azo group have greater affinity and bonding energy for the film than ortho-hydroxyazo dyes. It is therefore expected that they will have better fastness to water. This has been substantiated by desorption experiments. The ortho-hydroxyazo dyes have, on the other hand, better fastness to light and the presence of carboxyl or sulphonic group in the benzene nucleus increases the light fastness considerably. The O-methyl ether of Orange I, which can exist only in the azo and not the hydrazone structure, has much better light fastness than the parent hydroxy compound. It has also been observed that the presence of one sulphonic group in the molecule is best for dyeing the anodic film and when the number increases to three, both the speed of dyeing and the amount sorbed appreciably fall. It may be possible to select dyes suitable for practical dyeing if this knowledge is applied. Dyed aluminium may be required only for a class of

work where only a particular fastness property will be required e.g. household articles will require good fastness to washing. It may be found that an azo dye with one sulphonic group and a para-hydroxy azo structure group is suitable for such a purpose. Evaluation of affinities, particularly for the undyed film (at the start of the process) may help as a guide to choice of mixtures of dyes having different orders of affinities at different concentrations. By further work on equilibrium sorption of dyes on anodic film and consideration of the data with the help of thermodynamics, it may be possible to relate the affinities and entropy changes to the structure of the dye molecule which will then enable the chemist to design dye molecules with the most satisfactory properties for the purpose required.

We wish to point out here that the present work should be regarded as preliminary. A more extensive investigation of the problem might be necessary to elucidate fully the complex processes involved. The literature on the dyeing of textile fibres should serve as a guide in such work.

Summary and Conclusions.

At the start of the work, sorption tests of dyes on anodic film produced in sulphuric acid electrolyte were made. Perhaps due to the impurity of the film, very reliable results could not be obtained. This work, however, indicates that at higher temperatures (near the boil) the regularity in sorption broke

down and very erratic results were obtained. The observations made on lake-forming dyes were confirmed later when work on chromic acid film was done.

The anodic film formed in chromic acid electrolyte is considered to be more suitable, as the film is reported to consist of practically pure aluminium oxide.

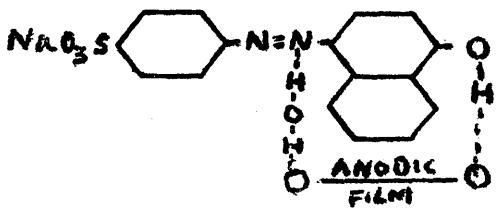
The rates of sorption of Solway Blue BNS and Alizarin Red 1P showed that a definite chemical combination takes place between the dye and the film. The calculations of the number of molecules of dye combining with one of the aluminium oxide do not lead to any conclusion, no doubt because only a part of the anodic film is accessible to the dye molecules, depending on their size. The structure of the metal-dye complex is discussed from the point of view of the electronic theory of valency. It has been suggested that the co-ordinate link between the metal atom and the oxygen (of the carbonyl group in this particular case) is electrostatic in nature and not co-valent as suggested by Sidgwick and others. The structure of the complex based on this conception is indicated and the electrostatic bond is represented by a red arrow with heads at both ends.

The rate of sorption of Tartrazine O at four temperatures showed that the higher the temperature the lower is amount sorbed at equilibrium, which is analogous to the effect of temperature in physical adsorptions. The curves in which the amount sorbed is plotted against the square root of the time,

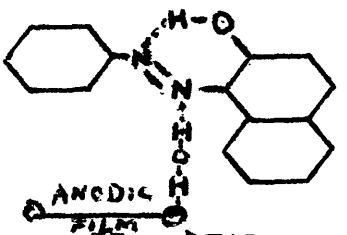
however, indicate that the process may involve a diffusion and that the film probably consists of two or three layers each having a different diffusion constant, which result in curves broken up into two or three straight lines.

The study of the kinetics of sorption of Orange I, Orange II and Azo Geranine 2G has shown that the effect of rise of temperature on sorption is to increase the rate of sorption, but to decrease the equilibrium sorption. Curves in all the three cases suggest diffusion in more than one layer, as in the case of Tartrazine O. Diffusion constants have been calculated for all the three dyes for four temperatures. They range from 10^{-12} to 10^{-16}, which when compared with the average diffusion constants of dyes in water (10^{-6}) indicates that the diameter of the pores must be nearer 10 Å than 100 Å, these being the two different values reported in the literature. From the values of diffusion constants, the calculated values of amounts diffused after various periods of time were obtained with the help of the diffusion equation developed by Hill, and these were compared with the observed values. The two sets of values agree fairly well in all cases. Therefore it is suggested that the dyeing of anodised aluminium is mainly a diffusion process. On applying the Langmuir equation to the rate data, it was found that this equation is not obeyed. The rate data were also used to calculatedthe energies of activation of all the three dyes with the help of Arrhenius equation. The implications of the values so obtained have been discussed.

Equilibrium sorption values were obtained for the three dyes at 25°, 40°, 60° and 80°C and the isotherms constructed. The isotherms in all the cases are straight lines passing t through the origin. This suggests that the process of sorption is probably a solution of dye in the film. The application of Langmuir's formula to the equilibrium data results in straight lines, but an attempt to calculate the constants involved in the formula led to absurd values being obtained. It is therefore concluded that the Langmuir conception of adsorption is not applicable in these cases. Energy changes involved in the process are next considered and a formula to calculate the standard change in chemical potential ($\Delta\mu^0$) or standard free energy change, which is a measure of the affinity of the dye for the film, is developed. The mean affinity of Orange I is higher than that of Orange II or Azo Geranine 2G, which have almost equal values. The heats of reaction calculated from the Van't Hoff's isochore are 12.0 K.cal. for Orange I and 8.0 K.cal. for Orange II and Azo Geranine 2G. This suggests that there are three hydrogen bonds involved in attachment of Orange I to the anodic film and two in the case of Orange II and Azo Geranine 2G. The modes of attachment are postulated as



Orange I ⟶ Film



Orange II ⟶ Film

(The mode of attachment of Azo Geranine 2G is supposed to be of the same nature as Orange II and is not shown). The desorption experiments confirm the expectation from this that Orange I should be faster than Orange II and Azo Geranine 2G. The values of entropy changes calculated from the available data support the view that in the case of Orange I the dye molecule has much less rotational and translational freedom than Orange II and Azo Geranine 2G. The relative affinities for undyed film have been calculated from an equation developed from the consideration of free energies involved. The values of the affinities at two concentrations, representing a range that is encountered in practice, show that the order of affinities changes with concentration, depending upon the basicity of the dyes concerned. It is suggested that these considerations become important when mixtures of dyes possessing different affinities are used in dyeing practice.

Sorptions of simple organic compounds - phenol and o-nitrophenol from aqueous solution, benzeneazo-α-naphthol, benzeneazo-ß-naphthol, and azobenzene, from dry benzene, were attempted. Phenol was sorbed and o-nitrophenol was not sorbed. The heat of reaction of phenol was found to be 5 K.cal. The sorption of benzeneazo-α-naphthol appeared to be merely on the surface and obeyed the Langmuir equation. The heat of reaction was, however, found to 4.0 K.cal. which suggested the formation of one hydrogen bond. Benzeneazo-ß-naphthol was not sorbed from dry benzene, and also not from aqueous alcoholic solution. This suggested

that the other nitrogen atom of the azo group does not form a strong hydrogen bond unless an acid group such as $-HSO_3$ is present in the benzene nucleus. The first part of this hypothesis has been confirmed by the work of others in these laboratories. Azobenzene was not sorbed from benzene solution, but was sorbed from aqueous alcohol solution, suggesting that the link was formed between it and the film through a water molecule.

The observation that "donor" compounds such as nitrobenzene, anthraquinone, ß-naphthoquinone, etc., were not sorbed from benzene solutions confirmed the assumption that aluminium oxide of the anodic film has no hydrogen atom available to act as an acceptor of a bond. The sorption of these donor compounds from benzene solutions in the presence of hydroquinone but not in presence of phenol indicated that dihydroxy compounds like this can act as bridges in sorption of one donor compound on another donor compound, such as the anodic film.

The action of hot water in "sealing" the film is considered. The water taken up by the film is divided into two types, - loosely held and tightly bound. The former is easily lost, while the latter is not removed even at high temperatures.

The reason why basic dyes do not dye the film is shown to be due to the positive <u>zeta</u> potential of the film.

The mechanism of hydrogen bond formation from the point of view of resonance among various structures of the aluminium oxide molecule is discussed. The light fastness observations

have also been included and discussed.

The practical aspects of the work have been indicated.

A physical picture of the dyeing process may, therefore, be presented as follows:-

(1) When mordant dyes are sorbed on the film, lake formation takes place.

(2) When an anodised foil is dyed with an acid dye, first the dye anions are attracted to the film surface by virtue of their negative charge. The dye then diffuses inside the pores of the film, ultimately becoming attached by hydrogen bonds. The dyes which do not have a free hydrogen atom in the structure to act as acceptor, form a bridge with the help of water molecules present in the solution.

APPENDIX.

APPENDIX.

The experiments described below constitute an earlier phase of the work, which was done as a preliminary study of the processes involved. The earlier portion refers to the work of anodising in sulphuric acid electrolyte and was reported in the A.R.T.C. Thesis (48). The latter part refers to chromic acid electrolyte.

1. Sulphuric Acid Electrolyte.

The anodising cell and the electrical circuit are the same as described earlier for the chromic acid process. Here will be studied the effect of variations of the conditions of anodising.

(a) Variation of time of anodising.

Keeping all the other conditions the same, the time of anodising was varied and ten readings taken in each case to measure the amount of oxide formed. The results obtained have been put in Table I as percentage of oxide formed as average of ten readings.

Table I.

OPERATING CONDITIONS	15°C. C.d. 8 amp/sq.ft. Electrolyte 11% H_2SO_4				
	Time in mins.	15	30	60	120	240
Wt.of $Al+Al_2O_3$ (mgrms)		113.6	114.2	120.6	120.5	122.1
Wt.of Al (mgrms.)		104.7	97.2	89.5	62.9	17.8
Wt.of Al_2O_3 (mgrms.)		8.9	17.0	31.1	57.6	104.3
% $Al_2O_3/Al+Al_2O_3$		8.0	14.9	25.7	47.8	85.4

(b) Variation of temperature of electrolytic bath.

In this experiment the temperature of the electrolytic bath was raised and the amount of oxide formed for two different timings was estimated. In this case also ten readings were taken and the average of the results obtained is expressed in Table II.

(c) Variation of current density.

This time current density was raised, keeping all other conditions constant and amount of oxide formed was determined as before. The results are contained in Table III.

Table II.

OPERATING CONDITIONS	C.d. 8 amp/sq.ft. Electrolyte 11% H_2SO_4					
	Time	1 hour			2 hours	
	Temp.	15°C.	25°C.	35°C.	15°C.	25°C.	35°C.
Wt.of $Al+Al_2O_3$ (mgrms)	120.6	110.7	87.8	120.5	93.7	51.3
Wt.of Al (mgrms.)	89.5	88.0	73.9	62.9	65.1	44.0
Wt.of Al_2O_3 (mgrms)	31.1	22.7	13.9	57.6	28.6	7.3
% $Al_2O_3/Al+Al_2O_3$	25.7	20.5	15.8	47.8	30.5	14.2

Table III.

OPERATING CONDITIONS	25°C. 1 hour. Electrolyte 11% H_2SO_4	
	C. d.	8 amp/sq.ft.	18.3 amp/sq.ft
Wt. of $Al+Al_2O_3$ (in mgrms.)	110.7	99.6
Wt. of Al (in mgrms.)	88.0	33.2
Wt. of Al_2O_3 (in mgrms.)	22.7	61.4
% $Al_2O_3/Al+Al_2O_3$	20.5	61.3

(d) Effect of different variables.

The above results clearly show the large effect that different variables have on the ultimate result of anodising. The effects can be summarised as expressed in Table IV.

Table IV.

Constant	Variable	Effect on oxide formation.
Electrolyte, c.d., time	Temp.	Decreases with increase in temp.
Electrolyte, time, temp.	C.d.	Increases with increase of C.d.
Electrolyte, C.d., temp.	Time	Increases with time.

2. Chromic Acid Electrolyte.

The aluminium foil was anodised by the standard method described earlier in this thesis. The amounts of oxide formed on a 2" x 1" piece (which was used for all sorption work) were estimated by using the stripping solution prepared from phosphoric acid and chromic acid. The proportions have been given earlier. The following table contains the mean values of three sets of readings taken.

Table V.

Amount of oxide on 2" x 1" strip formed in chromic acid electrolyte.

Wt. of $Al+Al_2O_3$ mgm.	Wt. of Al mgm.	Wt. of Al_2O_3 mgm.	$\frac{\% Al_2O_3}{Al+Al_2O_3}$
177.1	134.6	42.5	24.0
181.5	138.8	42.6	23.5
179.3	138.9	40.4	22.6
169.7	127.1	42.6	25.1
179.3	134.4	44.9	25.0
184.5	144.1	40.4	22.0
	Mean	42.2	23.7

The thickness of the film was 8.5 μ .

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